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No. 1.

EHRLICH'S CHEMOTHERAPY.*

By HENRY P. TALBOT.

Chemotherapy has been called "a new science." It should, rather, be regarded as the designation of a scientific field in which therapeutics and chemistry intermingle in the solution of problems involving the principles of both of the older sciences, much as do physics and chemistry in so-called "physical chemistry," which is not, on that account, regarded as a "new" science.

Therapeutics is defined as that branch of medical science "which deals with the composition, application, and modes of operation of the remedies for disease." But it has now taken on a somewhat broader, though less exact, meaning, and is understood to include the general administration of medicine, questions of hygiene and dietetics, and much that has to do mainly with the general well-being of the individual. That chemistry must be, as it has been for centuries, inseparable from the study of therapeutics is obvious, and the advance from the simplicity of the theory of Geber, according to which the animal organism was made up of only "sulphur" and "mercury" to our still very imperfect knowledge of the complex changes of physiological processes is, indeed, remarkable. But modern medical and chemical science is not content with the mere alleviation of the ravages of existing disease, that is, with the modifying or assisting of functions temporarily disturbed, but has struck more directly at the root of the trouble by devising means actually to destroy the causative agents and thus arrest the disease, or to render the animal organism inhospitable to these causative agents, as, for example, through the anti-toxins and the methods of preventive medicine in general.

All this had been done even before the advent of chemotherapy. What, then, is new about this combination of scientific effort in two allied fields? Essentially this: It is a logical, systematic campaign against diseases which are caused by the infection of the animal organism by parasites (i. e., bacteria or protozoa) by means of chemicals which have not been found by empirical and more or less haphazard methods, but have been synthesized and built up solely for the purpose in hand, and as the result of

researches which have called for the highest type of accurate observation and analytical reasoning for their execution. In this way it has been found possible to devise means by which the animal organism can be sterilized with respect to the parasites in question, and the consequent symptoms of disease can be arrested.

The development of this field is due almost entirely to Professor Paul Ehrlich, of Frankfort, and his co-workers. Dr. Ehrlich was educated as a physician, but has now become also one of the most accomplished and able investigators in the field of synthetic organic chemistry. A conception of the significance of his work can, perhaps, be best obtained by noting important phases in its progressive development.

More than thirty years ago Ehrlich began using coal-tar colors in his physiological studies, employing them as stains for preparations to be examined under the microscope. It is, of course, now commonly known that certain dye-stuffs appear to have a selective affinity for certain tissues of the body, or for certain parasites when residing within it, and these stains are in every day use by the pathologist. But it was not so thirty years ago, and Ehrlich first found that a dye-stuff known as methylene-blue, and its congeners, were the only colors which would stain live nerve tissue, and drew from this the important inference, which is at the basis of chemotherapy, that this was because of a particular receptivity for these dye-stuffs on the part of these tissues or parasites. It is easy to understand something of the importance of this use of these stains, or dyes, if it is recalled that the changes produced in the individual cells or tissues by drugs are not detectable even under the microscope in most cases, and that it is only through these stains that a knowledge of what has actually happened can be even approximately learned.

Ehrlich concluded from his observations that it was probable that, since these tissues and parasites possessed this receptivity for these specific bodies, there must be some definite effect produced as a result of the combination, if combination it were, and proceeded to conduct investigations in this direction. After some time these researches were rewarded, and in 1890 Ehrlich and Lapmann published a paper on the pain-relieving properties of methylene-blue, and, later, Ehrlich and Guttmann found that the same dye

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was fatal to one type of the plasmodium, the parasite which causes malaria. As the latter field of investigation, that of the effect upon parasites, appeared very promising, they turned their attention to a particular class of parasites known as trypanosomes, because these could be more easily studied by the inoculation of mice.

The disease-producing parasites are sometimes of vegetable origin, as the bacteria, and sometimes of animal nature, as the protozoa. The trypanosomes are worm-like bodies, somewhat larger than bacteria, belonging to the animal class, and the diseases which they produce prevail most generally in tropical countries. Of these diseases, surra, most generally known in India among cattle, dogs and camels; nagana (tsetse-fly disease), known in Africa among animals in general; and mal de cadaras, known in South America among horses, are typical, while man is also attacked by the sleeping sickness in the tropics. The scourge of syphilis is produced by a parasite known as the spirochete, which is closely allied to the others named, although it is still undetermined whether its nature is animal or vegetable. As will be seen, this particular disease has been found to be one of the most amenable to treatment.

As a result of his researches, Ehrlich formulated a theory regarding the behavior of the cells of living tissue, or of parasites toward foreign bodies. He conceives them as made up of a central "dominant body," which throws out "sidechains," to which he later gave the name receptors. These are of variable character, some being nutrient receptors, and others chemo-receptors, that is, receptors for certain definite chemical elements or groups of elements, known in chemistry as radicals. In a crude sense, the receptors may be likened to locks, and the nutrient or chemical bodies as keys, each fitting a particular lock. as, for example, the dye-stuff methylene-blue already mentioned. The combinations thus affected may be beneficial to the cell, as in the case of the nutrients, or they may result in the poisoning and death of the cell, as in the case of the methylene-blue when brought into contact with the type of plasmodium referred to above, or quinine for plasmodia in general, a specific remedy for malaria discovered by empirical research.

Ehrlich and his co-workers, with extraordinary skill and industry, prepared several hundred dye-stuffs, studying the varying effects of alterations in chemical structure, each new compound having been logically selected as the result of laboratory tests of its parasitocidal efficiency. Of all these, very few finally withstood severe tests, possibly not more than ten in all, but the fact was established that it was possible in certain cases to sterilize the animal organism with respect to parasites, by this means, without, at the same time, poisoning the animal itself. They were also able to establish certain principles as to the chemical structure of the dye-stuffs most likely

to be effective. They encountered, however, many difficulties. A dye which would attack and destroy a given parasite in a particular animal would not always do so in another species. Symptoms of disease would sometimes recur after varying intervals, and the parasites would then often exhibit peculiar resistance to further attack.

While these researches were still in progress, Uhlenmuth and Salmon published an account of instances of marked success in the destruction of the spirochete of syphilis, and the arrest of the disease, by the use of an arsenical compound known as atoxyl. Secondary and seriously harmful effects to the patients were, however, the consequence of this treatment, but the parasitocidal properties of this compound were so marked that Ehrlich turned his attention to it, in an attempt to so modify its effects upon the animal organism which was harboring the parasites, that its curative power might be made available.

The task was by no means a simple one. He first established the composition of the atoxyl as a para-amido-phenyl arsenic acid. The vast amount of work already done with the dye-stuff indicated certain lines of probable success, which, nevertheless, was only attained on the synthesis of the six hundred and sixth organic compound by Ehrlich and Kata, sometimes known as "606," and now designated salvarsan. Chemically it is dioxy-diamido-arseno-benzol, in which arsenic is associated with structural groups akin to those found in the dye-stuffs. A later preparation, "914," known as neo-salvarsan, is said to be a combination of a salvarsan with sodium formaldehyde sulphoxalate, which is designed to overcome a certain difficulty in administration of the salvarsan, due to acidity of its solutions.

Ehrlich assumes that the parasite of syphilis, the spirochete, possesses among others, arsenio-receptors, and that through the combination with this arsenic compound the parasite is poisoned and dies. Ehrlich claims that in more than twelve thousand cases in which this drug has been administered by him, no single case of poisoning has resulted. The administration of the drug, which is intravenous, or intramuscular, requires, however, considerable skill and care. The treatment with salvarsan is often combined with that of mercury. There seems to be no doubt that this preparation exerts a specific and destructive action upon the spirochete, and has already resulted in the alleviation of an enormous amount of suffering (often hereditary and undeserved) from this dreadful scourge. It is still too early to make final statements as to the permanence of the cures affected although there is much reason for hopefulness. It should, however, be noted that this chemotherapeutic treatment, unlike the anti-toxin treatment for certain other diseases, does not at all produce immunity from later infection from the same disease. Indeed, there is some evidence to show that

cases of re-infection are distinctly harder to treat successfully than those of initial infection. The cure of advanced cases of the disease naturally presents greater difficulties, because of secondary disturbances of the vital organs, but many of these have been materially alleviated.

The progress made in the chemotherapeutic treatment of diseases produced by other trypanosomes, notably that of the "sleeping sickness," has been less marked up to the present. Something has been gained, but no specific drug comparable with salvarsan in its efficiency has yet been found.

It is, however, recorded that in Surinam a hospital was established to treat cases of another tropical disease known as the yaws. In the course of eight days three hundred and twenty-eight cases were admitted, and at the end of fourteen days the last patient was discharged, cured, and the hospital had to be closed.

In another field the work of Ehrlich has led to procedures which are of the greatest promise in the study of the processes involved in the progress of medical and physiological research, namely, so-called "vital staining." By means of the injection of dye-stuffs into living organisms, it is possible, because of the selective receptivity of certain tissues or parasites, for a particular color, to trace the movement of bacilli, and to watch the changes which they occasion in the living organism itself. The same procedure is employed in the study of healthy tissue.

To Ehrlich's clear, analytical mind, exceptional executive ability, fine technique, and extraordinary industry is due not only the procedure by which certain particular diseases may be arrested, but a splendid example of logical attack upon other similar problems, which offers great promise for the future, even though, as in the case of the anti-toxins, one marked success may not be at once followed by others of equal moment. He has demonstrated, in a way which cannot be detailed in the scope of this article, that the test-tube experiments made in the laboratory with a particular drug upon a special parasite cannot be alone relied upon as an index of the effect upon it of the same drug when it is harbored by the living organism, since the action is essentially modified by that organism, and he has advanced theories which at least help in the understanding of the possible reasons for the variations in behavior thus observed. Even though Ehrlich's chemotherapy may not be, in an exact sense, a "new science," it must be acknowledged to be a most fruitful and helpful combination of the principles of two well-recognized and time-honored sciences for the benefit of mankind.

The consumption of fuel oil this year by the United States Navy is estimated at 30,000,000 gals.

TENTATIVE SPECIFICATIONS AND ANALYTICAL PROCEDURE FOR 30 PER CENT HEVEA RUBBER INSULATING COMPOUND.

A conference of manufacturers and users of rubber insulation was held at New York on Dec. 7, 1911, upon the invitation of Mr. E. B. Katte of the N. Y. C. & H. R. R. Co. The following interests participated: U. S. Signal Corps, U. S. Bureau of Standards, American Chemical Society, New York Central Lines, Pennsylvania R. R., General Electric Co., Hazard Manufacturing Co., Simplex Wire & Cable Co., Standard Underground Cable Co. Major S. Reber, of the U. S. Signal Corps, was elected chairman.

Attention was called to the diversity of the specifications and methods of analyzing rubber insulation then in vogue, and it was suggested that steps be taken to improve and standardize them. After full discussion, it was decided to appoint a committee to devise specifications and an analytical procedure for rubber insulating compounds. The following report of this committee, which is known as the Joint Rubber Insulation Committee, is taken from the Journal of Industrial and Engineering Chemistry:

The committee has consulted the available literature on rubber analysis and has also obtained assistance and advice from chemists interested in this field of work. Some of the details in the methods of analysis were taken directly from the work of others when such action was warranted by the experimental results obtained, and in certain cases modifications were made in available methods. In some cases the methods adopted constitute distinctly new features in rubber analysis.

The committee desires to express its thanks, especially to Messrs. D. A. Cutler, F. Dannerth, F. S. Deemer, F. A. Hull, M. M. Kahn, G. H. Savage and D. Whipple.

W. A. DEL MAR,

P. POETSCHKE,

E. L. WILLSON,

Sub-Committee on Publication of Report.

PART I. GENERAL REPORT.

At the conference of Dec. 7, 1911, it was resolved that a committee be appointed to develop a means of specifying and analyzing rubber insulation, the committee to report its findings at a future conference.

The chairman of the conference, assisted by other members, appointed the following to serve upon this committee: C. R. Boggs, Simplex Wire & Cable Co.; W. S. Clark, General Electric Company; W. A. Del Mar, W. B. Geiser, N. Y. C. & H. R. R. Co.; J. P. Millwood, consulting chemist; P. Poetschke, Lederle laboratories; H. B. Rodman, Pennsylvania R. R. Co. Later, at the request of the committee and by unanimous consent of the members of the original conference, the following were added: J. B. Tuttle, U. S. Bureau of Standards, and E. L. Willson, Hazard

Outline of Procedure.—The general procedure is shown by the diagram Fig. 1, which gives an outline of the separations to be affected by acetone and chloroform extractions, and saponification with alcoholic potash.

General.—Make the analysis upon the insulation after vulcanization and, whenever possible, before the saturation of the braid. Wipe the insulation thoroughly with a damp cloth to remove any adhering material, but do not remove waxy hydrocarbons from the surface.

If, however, a saturated braided sample must be used, remove the braid and sandpaper the insulation to a depth of at least 5/1000 of an inch and wipe with a damp cloth. In such cases report the condition of the sample.

Perform all determinations in duplicate and take the average value arbitrarily as the true value. Duplicate determinations must check within the limits specified.

Make blanks on all determinations and deduct the result accordingly.

Sample.—Remove the insulation entirely from sufficient wire to give a sample weighing about 25 grams. Cut this into small strips and grind slowly in either a No. O Enterprise coffee mill or a mill such as shown by the diagram Fig. 2. Adjust the grinder so that not more than 20 per cent will pass through a 40 mesh sieve. Sift all the material through a 20 mesh sieve, regrinding what is retained on the sieve until the entire sample has passed through. The wires of the sieve shall be evenly spaced in both directions and shall be of 0.016 and 0.010 inch diameter in the 20 and 40 mesh sieves, respectively. Remove with a strong magnet any metal that may have come from the grinder and thoroughly mix the sample.

Extraction Apparatus.—The extraction apparatus shall conform with the diagram Fig. 3. It shall be heated so that the period of filling an empty cup with acetone and completely emptying it will be between $2\frac{1}{2}$ and $3\frac{1}{2}$ minutes.

Preparation for Reagents.—Acetone shall be freshly distilled over anhydrous K_2CO_3 , using the fraction $56-57^\circ C$.

Alcoholic KOH solution shall be of normal strength and shall be freshly made by dissolving the proper amount of KOH (purified by alcohol) in 95 per cent alcohol which has previously been distilled over KOH. The solution shall be allowed to stand for 24 hours and only the clear liquid used.

Ether shall be washed with three successive portions of distilled water and distilled, using the fraction $34-36^\circ C$.

Chloroform shall be pure and freshly distilled.

Carbon tetrachloride shall be pure and freshly distilled.

Reagents not otherwise specified shall be C. P.

Acetone Extraction.—Extract continuously with 60 c.c. acetone for eight hours, two 2 g. samples that

have been prepared within 24 hours. Unite the extracts in a weighed flask, using hot chloroform to rinse the flasks. Distill off the reagents and dry the flask and contents for four hours at $95-100^\circ C$. Desiccate until cool and weigh. Continue to dry for 2 hour periods until constant weight is obtained. In drying, place the flask on its side but at a sufficient angle from the horizontal so that the extract does not appreciably run down the side of the flask.

Unsaponifiable Material.—Add to the acetone extract 50 c.c. alcoholic KOH solution, boil under a reflux condenser for two hours, and evaporate to dryness, removing all alcohol. Add 10 c.c. water and 20 c.c. ether, heat until the wax, etc., are in solution; cool, transfer to a separatory funnel, wash out the flask with warm water and, when cool, finally with two 20 c.c. portions of ether. The water volume

RUBBER ANALYSIS EXTRACTION APPARATUS

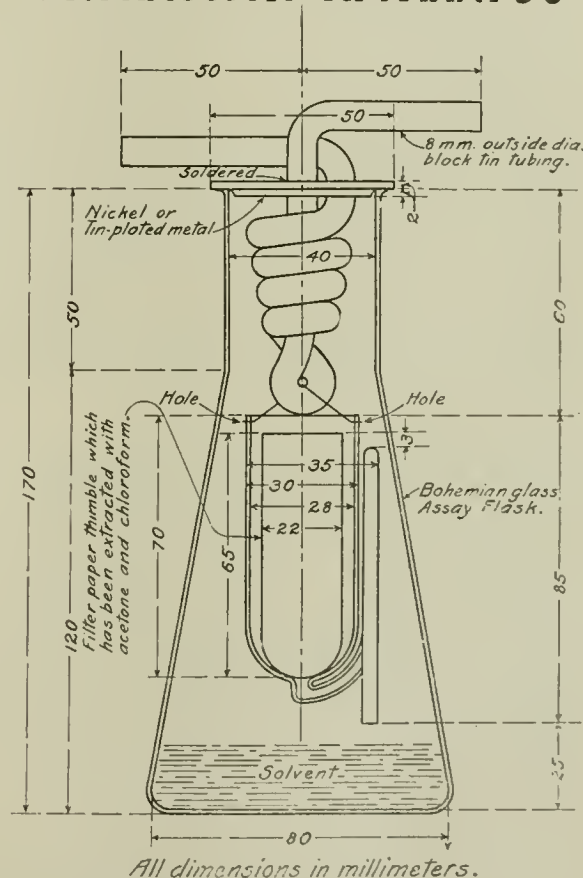


Fig. 3—Extraction Apparatus.

should be 100 c.c. and the ether at least 40 cc. Shake vigorously for two minutes, and allow the solutions to separate thoroughly. Draw off the aqueous solution into a second funnel, leaving in the first funnel the ethereal solution and any flocculent material that may be present. Again rinse the flask with 20 c.c. ether and add it to the aqueous solution; shake vigorously for two minutes, and when separated draw off the aqueous solution and unite in the first funnel the ethereal solutions and any flocculent material. Repeat, shaking with 20 c.c. portions of ether until the

extraction is complete, using at least 120 c.c. ether. Wash the flask and the funnel, from which the ethereal solution has been taken, with water, until they are free from alkali, subsequently using this wash water to wash the ethereal solution. Continue washing with water until it has been washed twice after it shows no alkaline reaction. Retain with the ethereal solution and flocculent material. Filter the ethereal solution from the flocculent material, through a small pellet of extracted cotton, into a weighed flask, washing first with ether and subsequently with hot chloroform, using this to rinse the original flask and both separatory funnels. Evaporate the solvents and dry the extract to constant weight at 95-100° C.; desiccate until cool and weigh.

Hydrocarbons A.—Add 50 c.c. absolute alcohol to the unsaponifiable material and warm until solution is as complete as possible. Cool the solution to -4 or -5° C. and maintain at this temperature for one hour by packing the flask in a mixture of ice and salt. Filter out the waxy hydrocarbons, using a funnel packed with ice and salt, and apply suction if necessary. Wash the flask and filter with about 25 c.c. of 95 per cent alcohol, which has been previously cooled to the same temperature. Catch the filtrate in a flask which is afterwards cooled to -4 or -5° C. to make sure that all possible waxy hydrocarbons have been removed, and refilter if necessary. Dissolve the residue on the filter paper with hot chloroform, into the original flask. Evaporate the chloroform and dry the flask to constant weight at 95-100° C.; cool in a desiccator and weigh.

Hydrocarbons B.—Evaporate the alcohol from the flask containing the alcohol-soluble unsaponifiable material, add 25 c.c. carbon tetrachloride and transfer to a separatory funnel. Shake with conc. H_2SO_4 , drain off the discolored acid and repeat with fresh portions of acid until there is no longer any discoloration. After drawing off all the acid wash the carbon tetrachloride solution with repeated portions of water until all traces of acid are removed. Transfer the carbon tetrachloride solution to a weighed flask; evaporate off the solvent and dry the flask to constant weight at 95-100° C. Cool in a desiccator and weigh.

Free Sulphur.—Add two grams KNO_3 to the aqueous solution and washings from the ethereal separation of the unsaponified material. Evaporate to dryness in a silver or nickel dish and heat to quiet fusion, avoiding contamination with sulphur fumes. Transfer with water to an evaporating dish, acidify with HCl , evaporate to dryness, and dehydrate silica. Add 2 c.c. conc. HCl , take up in water, filter and wash, making a volume of 200 c.c. Heat to boiling and add slowly a slight excess of hot 10 per cent BaCl_2 solution. Allow to stand over night, filter, wash, ignite, weigh the BaSO_4 and calculate to sulphur.

Definition of Terms Describing Components of Acetone Extract.—The difference between the Ace-

tone Extract and the Free Sulphur shall be called the *Organic Extract*.

The difference between the Organic Extract and the Unsaponifiable Material shall be called the *Saponifiable Acetone Extract*.

The sum of the Hydrocarbons A and B, shall be called the total *Waxy Hydrocarbons*.

The difference between the Unsaponifiable Material and the Waxy Hydrocarbons shall be called *Unsaponifiable Resins*.

Chloroform Extraction.—Extract continuously the residue from one of the acetone extractions (without necessarily removing the acetone that may be on it) for four hours with 60 c.c. chloroform, using a weighed flask. Distill off the solvent and dry the flask and contents for two hours at 95-100° C. Desiccate until cool and weigh. Continue to dry for one hour periods until constant weight is obtained. In drying, place the flask on its side but at a sufficient angle from the horizontal so that the extract does not appreciably run down the side of the flask. (If it is needful to wait after the acetone extraction, before starting the chloroform extraction, the sample must be kept in a vacuum of at least 50 mm. of mercury.)

Alcoholic Potash Extraction.—Dry the residue from the chloroform extraction at 50-60° C., put into a 200 c.c. Erlenmeyer flask with 50 c.c. alcoholic KOH solution and boil for four hours under a reflux condenser. Filter the solution into a beaker and wash twice, using each time 25 c.c. hot absolute alcohol and then wash thoroughly with hot water. Evaporate the solution to approximate dryness, take up in warm water and transfer to a separatory funnel. Acidify with 15 c.c. 5 N HCl , using this to rinse the beaker. Add sufficient water to make the bulk of the solution 100 c.c. When cool add 40 c.c. ether, using it to rinse the beaker in 20 c.c. portions. Shake the aqueous and ethereal solutions thoroughly. After complete separation, draw off the aqueous solution and treat in another separatory funnel, with a fresh 20 c.c. portion of ether. Continue to shake the aqueous solution with fresh portions of ether until a colorless portion has been obtained, then shake out twice more. Unite the ethereal solutions and wash with successive additions of water, continuing twice after the water shows no acid reaction. Filter through a plug of extracted cotton into a tared flask, wash the filter and funnel with ether, evaporate the ether without boiling and dry the residue to constant weight at 95-100° C. Cool in a desiccator and weigh.

Fillers.—Extract a 1 g. sample with acetone for five hours. Transfer the residues to a tall 200 c.c. lipped beaker, add 40 c.c. terebene and 20 c.c. xylol and heat on an oil bath at 105-110° C. for about 20 hours, or until the bulk of the fillers settle promptly after stirring. Occasional stirring will aid the solution. Allow the beaker to stand until the fillers and undissolved residue have settled thoroughly and decant the supernatant solution into a beaker. Add to the undisturbed

residue 30 c.c. terebene; heat for several hours, allow to settle, decant, unite the decanted solutions and repeat this treatment as long as there is any indication of rubber being present. Continue to heat the decanted solutions during the further treatment of the undissolved residue and filter them through a tared filter paper. This filter paper must be of close texture and shall have been washed with terebene, alcohol and acetone. The tare filter shall be treated with the same solvents and dried in the same manner throughout the analysis as the filter containing the residue. Weigh all filter papers in weighing bottles of sufficient size to take them without folding. Refilter if mineral matter runs through. Wash the beaker that contained the decanted solutions and the filter paper, with benzol, using a second beaker to catch the filtrate. Add benzol to the beaker containing the residue, heat and after settling decant, repeating this treatment with benzol until it is thoroughly washed. Filter and wash well with benzol. Wash in the same manner both beakers with hot alcohol and then transfer the residues to the filter paper, using hot alcohol and an acetone extracted policeman. Wash finally with acetone. Dry in air at 95-100° C. and weigh. Again wash the filter paper and contents with benzol and alcohol, dry, weigh and repeat this treatment until constant weight is obtained. Evaporate all the filtrates and washings, transfer to a porcelain dish, burn off and weigh. Add this amount to the fillers found above. If this ash is greater than 1 per cent, the entire determination shall be repeated. Subtract 0.5 per cent as an arbitrary value for the amount of organic matter from the rubber retained with the fillers.

Sulphur in Fillers.—Transfer the fillers from the filter paper into an iron crucible; burn the filter paper and add the ash to the crucible. Add the total sulphur flux and proceed with the determination of sulphur as in the next paragraph. Subtract the percentage of sulphur found from the percentage of fillers to determine the percentage of fillers free from sulphur.

Total Sulphur.—Mix a 0.5 g. sample with 4 g. Na_2O_2 and 6 g. K_2CO_3 in a dry 15 c.c. iron crucible. Cover and heat gradually until the mixture fuses, proceeding cautiously as rapid heating will cause an explosion, and then bring to quiet fusion for 15 to 20 min. Apply the heat so as to avoid contamination with sulphur fumes. Rotate the crucible while the melt solidifies. When cool, put crucible and cover into a casserole containing 200 c.c. of water; add 5-10 c.c. bromine water and boil until the melt is dissolved. Allow the precipitate to settle, decant the liquid through a thick filter and wash the residue with hot water. Acidify the filtrate with HCl, evaporate to dryness and dehydrate silica; add 2 c.c. conc. HCl, take up in water, filter and wash, making the total volume about 400 c.c. Heat to boiling and add slowly a slight excess of hot 10 per cent BaCl_2 solution. Allow to stand over night, filter, wash, ignite, weigh the BaSO_4 and calculate to sulphur.

Specific Gravity.—The specific gravity shall be the ratio of the weight of a given volume of the rubber, to the weight of an equal volume of water, both at 20° C. Cut strips of the largest applicable size from the conductor and use about 5 g. for the sample. Determine the specific gravity in the usual manner by means of a specific gravity bottle. Care must be taken that no air bubbles adhere to the sample.

Checks.—Duplicate determinations shall check within the following limits expressed as percentages of the original sample:

Determinations.	Limits for checks.
Acetone Extract	0.10
Saponifiable Acetone Extract	0.10
Unsaponifiable Resins	0.10
Waxy Hydrocarbons	0.10
Free Sulphur	0.05
Chloroform Extract	0.10
Alcoholic Potash Extract	0.10
Fillers, free from Sulphur.....	0.50
Total Sulphur	0.10
Specific Gravity	0.01

Interpretation.—The Rubber shall be considered to be the difference between 100 and the sum of the Waxy Hydrocarbons, Total Sulphur and the Fillers (free from sulphur), expressed as percentages. If the Chloroform Extract is over 3.0 per cent of the rubber so calculated, subtract the excess from the Rubber. If the KOH extract is over 1.8 per cent of the rubber, as first calculated, subtract this excess also from the Rubber.

Carbon and Red Lead.—Heat about 1 g. of the sample with 30 c.c. conc. HNO_3 and 15 c.c. water. A black insoluble residue indicates the presence of carbon.

When the rubber is dissolved, in the fillers determination, the absence of any red particles indicates the absence of red lead. If red particles are present, dissolve another sample by the same method as for fillers, filter the solution into a Gooch crucible and wash thoroughly. Remove the felt and a residue to distilling flask, add HCl and distill over the chlorine liberated by the lead peroxide, absorbing the gas in a solution of KI and starch. Not more than 0.1 c.c. $\text{N}/10$ thiosulphate shall be required to titrate the iodine liberated.

Statement of Results.—The results of the analysis shall be stated in the following form:

	Per cent
Acetone extract	
Saponifiable acetone extract	
Unsaponifiable resins	
Waxy hydrocarbons	
Free sulphur	
Chloroform extract	
Alcoholic potash extract	
Fillers free from sulphur.....	
Total sulphur	
Rubber	
Color of acetone extract (60 cc. vol.).....	
Fluorescence in acetone extract solution (present or absent)	
Hydrocarbons A (consistency and color).....	
Hydrocarbons B (solid or liquid).....	
Color of chloroform extract (60 cc. vol.).....	
Carbon (present or absent).....	
Red lead (present or absent).....	
Specific gravity	

PART III. EXPLANATION OF PROCEDURE.

General.—The committee felt the more acceptable solution of its problem of drawing up a procedure which would give the percentage of rubber present in a compound with a reasonable degree of accuracy, to be the perfection and amplification of the difference method rather than the development of a direct method, which, if equally correct, might not inspire confidence because of the comparative novelty of its application to this purpose.

The most feasible means of limiting the kind of rubber was considered to be the determination of the saponifiable and unsaponifiable resins. These are fairly constant characteristics of the resins of Hevea rubber, and of compounds made from the same. Other methods, such as the determination of the saponification number and the optical activity of the resins, were thought to be impracticable.

The method as developed is applicable to the analysis of any pure rubber compound containing only mineral matter with or without ceresin or paraffin wax, regardless of the kind or amount of rubber, and can be used in conjunction with other specifications, provided the limits are changed to correspond with the amount and kind of rubber desired, and due consideration is given to interfering mineral matter. When applied to a compound without ceresin or paraffin wax the unsaponifiable acetone extract is the unsaponifiable resins.

The method has been definitely described, to make it certain that experienced chemists may obtain concordant results. The interpretation has been rigidly defined, obviating any ambiguity as to the meaning that will be assumed, even though this sometimes appears to be arbitrary.

Sample.—In order to obtain uniform results, the committee has established, by experiment, that a definite method of sampling has to be adopted and that for all extractions the sample must be reduced in a prescribed manner to at least an approximately similar degree of fineness. For this reason the procedure specifies a definite type of grinder obtainable in two forms, and also specifies definite sieves.

Extraction Apparatus.—The committee has proved that the extraction apparatus used by different chemists must be of exactly the same form and the same size. It was also proved that small samples in the apparatus give the maximum results and that the rate of extraction is dependent upon the amount of solvent and its temperature as it passes through the sample. The apparatus finally adopted combines the advantages of several forms that were studied and together with simplicity of operation and adjustment to uniform conditions, gives practically complete extraction when used as specified. A number of other variations that might have a possible effect upon the amount of extract were tried but their effects were found to be inappreciable.

Acetone Extraction.—The extraction is made within 24 hours of the preparation of the sample, so obviating any appreciable oxidation. Two samples are extracted and united, so that a larger amount of extract may be obtained for the subsequent separations, and the extraction apparatus kept within a convenient size. Hot chloroform is used to facilitate the complete transference of the extract. The flasks are placed on their sides when drying to hasten the emission of the solvent and thus reduce chance of volatilizing, through longer heating, some of the more volatile constituents of the extract. Drying *in vacuo* at room temperature does not remove all the moisture if paraffin is present and such drying with heat or at 100° C. in an inert gas, presents no practical advantage over the method given.

Separation of the Acetone Extract.—The method given was developed so that all the desired constituents could be determined in one sample.

Emphasis is laid on thorough extraction of the unsaponifiable material and the retention of the flocculent material with the ethereal solution. This latter material is not soluble in either ether or water, but it was proved that if such as was chloroform-soluble were included in the unsaponifiable material, the subsequent determination of the hydrocarbons would be more exact. A portion of this flocculent material is insoluble in chloroform.

The hydrocarbons are determined in two places, making an approximate separation between the solid and the liquid ones, if both are present. The first hydrocarbons (A) are those insoluble in the solvent at a low temperature. The presence of unsaponifiable resins in the solution prevents the more complete freezing out of the hydrocarbons, but the remainder is obtained after treatment of the resins with sulphuric acid. In this way, chance of loss through the action of the acid has been largely eliminated.

The method for free sulphur gives all the sulphur in the acetone extract with the exception of negligible amounts which may be in the unsaponifiable material. It was proven that the results agree with determinations made directly on other acetone extracts.

The saponifiable and unsaponifiable resins are obtained by difference.

Chloroform Extraction.—The chloroform extraction should be made at once after the acetone extraction, or the sample put in a vacuum, so as to avoid the danger of an abnormally high extract. When the extract is dried as specified, constant weight is obtained before any appreciable oxidation occurs. If bituminous substances are present, that portion which has not been extracted by the acetone will be largely soluble in chloroform and can be readily distinguished by its color. The amount of extract is also affected by the presence of uncured rubber and rubber of low degree of polymerization. A properly cured Hevea compound will always give a little extract with chloro-

form, which varies somewhat with the method and conditions of cure.

Alcoholic Potash and Extraction.—The alcoholic potash extraction is the usual saponification process for obtaining the fatty acids of rubber substitutes. The total amount of such substitutes is not obtained, but if any appreciable amount is present, the value will exceed that of the limit allowed. When no substitutes are present, this determination always yields a small amount of extract from Hevea rubber.

Fillers.—Since the rubber is determined by difference, it is necessary to determine the amount of fillers. Ashing the compound gives accurate results provided no volatile or decomposable fillers are included. This, however, cannot be assumed to be the case. The determination of fillers by using solvents to dissolve the rubber has always presented a difficult problem and it is only after a great many experiments that the committee can report a reasonably satisfactory method.

Many kinds and probably every class of rubber solvents were tried, with the result that some did not completely dissolve the rubber at low temperatures and ordinary atmospheric pressure; others appeared to dissolve the rubber but formed a colloidal solution holding some of the fillers which could neither be filtered nor centrifuged clear of mineral matter; the ones that did not present these difficulties consumed much time.

Terebene was found to be the solvent which would most completely dissolve the rubber and after continued heating would completely destroy the rubber in solution as such, and so break up the colloidal solution. Filtering out the mineral matter is then a comparatively simple process. The treatment with terebene must be performed in the presence of air to break up the colloidal solutions. A disadvantage of using terebene is the length of time required to obtain satisfactory solution. The speed is greatly hastened if at first xylol is used with the terebene. After decanting this solution, terebene is used alone. The rapidity of the action is also hastened by increasing the temperature. The specified gives reasonable speed without serious danger of carbonizing the rubber or of losing any of the fillers by decomposition.

It was proved that there is organic matter derived from the rubber, which is insoluble in the solvents and remains with the fillers. Without taking this into account, the fillers will appear high, and the rubber by difference, low. As this organic matter was proved to be largely proteid matter, and this was originally a part of the rubber, an allowance is made for it. This is the amount generally retained when the method is carried out as specified. It is possible, by centrifuging, to throw out of the solution a great deal more than this, and it is also possible to determine the approximate amount retained in each case, but the slight increase in accuracy does not justify the extra determination.

Most of the details of this procedure are self-evident, but it is probably worthy of note that the benzol solutions are filtered into a separate beaker, as otherwise the benzol is apt to precipitate, from the terebene solution, organic matter which may be mistaken for mineral matter or conceal mineral matter passing through the filter. The filtrates are ashed since traces of mineral matter are always found in them. Emphasis must be laid upon the necessity of conducting blanks on the solvents.

Sulphur in Fillers.—The sulphur in fillers is determined in order to calculate the rubber by difference. It is carried out only on the fillers contained on the filter paper, the sulphur in the ash from the filtrate and washings being negligible.

Total Sulphur.—Several methods for total sulphur were tried. The method given was found to yield accurate results.

Interpretation of Results.—Emphasis is laid on the method of calculating the results. The saponifiable acetone extract and the unsaponifiable resins are considered to be parts of the rubber. The chloroform and alcoholic potash extracts, when within the limits specified, are likewise so considered. It has been explained that the proteid matter with the fillers has been allowed for, since it is also a part of the rubber. The fillers are calculated sulphur-free, so that the sulphur will not be subtracted twice. No allowance is made for the ash in the raw rubber as it is considered to be negligible. This method of calculation has to be adopted if the rubber found is to agree with that originally put into the compound.

Moisture.—A determination of moisture is not given, as electrical tests will detect its presence if in excess. If electrical tests are required, the error introduced by the omission of this determination is very small.

NOTE.—With a procedure of this length it is impossible to explain every detail without undue elaboration and the committee wishes to point out that while to experienced chemists the procedure may seem overburdened by detail, yet every specified detail was found necessary in order that the conditions essential to accurate and consistent work might be reproduced by all chemists using the procedure. For this reason it is extremely important that all instructions be observed even if their significance is not perceived by the individual chemist. It will probably be found that even with the instructions properly observed, some experience will be needed to apply the method successfully.

PART IV. TENTATIVE SPECIFICATION FOR 30 PER CENT RUBBER COMPOUND.

A 30 per cent fine Para or smoked first latex Hevea rubber compound with mineral base shall be furnished. It shall contain only the following ingredients: Rubber, sulphur, inorganic mineral matter, and refined solid paraffin or ceresin.

It shall not contain either red lead or carbon.

The vulcanized compound shall conform to the following requirements, when tested by the procedure which forms a part of this specification.

(a) Results to be expressed as percentages by weight of the whole sample:

	Maximum	Minimum
Rubber	33	30
Waxy hydrocarbons	4	..
Free sulphur	0.7	..

(b) Results to be taken between the limits given in proportion to the percentage by weight of rubber found:

	Limits allowed	
	Maximum	Minimum
For 30 per cent Rubber Compound:		
Saponifiable acetone extract	1.35	0.55
Unsaponifiable resins	0.45	...
Chloroform extract	0.90	...
Alcoholic potash extract	0.55	...
Total sulphur (see note 3).....	2.10	...
Specific gravity	...	1.75
For 33 per cent Rubber Compound:		
Saponifiable acetone extract	1.50	0.60
Unsaponifiable resins	0.50	...
Chloroform extract	1.00	...
Alcoholic potash extract	0.60	...
Total sulphur (see note 3).....	2.30	...
Specific gravity	...	1.67

The acetone solution shall not fluoresce.

The acetone extract (60 c.c.) shall be not darker than a light straw color.

Hydrocarbons shall be solid, waxy and not darker than a light brown.

Chloroform extract (60 c.c.) shall be not darker than a straw color.

Failure to meet any requirement of this specification will be considered sufficient cause for rejection.

NOTE 1.—Contamination of the compound, such as by the use of impregnated tapes, will not excuse the manufacturer from conforming to this specification.

NOTE 2.—This specification shall be supplemented by appropriate clauses relating to tensile strength, elasticity, insulation resistance and dielectric strength.

NOTE 3.—The limit of total sulphur may be omitted at the option of the purchaser (see Part V).

PART V. EXPLANATION OF SPECIFICATION.

Experience has shown that compounds which upon analysis show the characteristics of good Hevea rubber, may be relied upon to be more permanent than those made of rubber of other grades. It is not affirmed by the committee that a compound which conforms with this specification, is necessarily permanent, or that a better compound cannot be made, but it is believed that enforcement of the specification will limit the use of inferior materials and that it will put the manufacturers more nearly upon an equality of endeavor, where they can use their experience to obtain the best results. Used in connection with the analytical procedure, the specification will enable purchasers to order a good compound and to ascertain with a greater certainty than heretofore, whether the material received represents the compound specified.

The term Hevea applied to rubber means rubber from the *Hevea Brasiliensis* tree whether wild or cultivated and regardless of the locality in which it has been grown. Para rubber is Hevea rubber which has been shipped from the port of Para, Brazil, and comes in several grades. Smoked first latex Hevea rubber is a high grade of plantation rubber which is collected prime and consists entirely of rubber which has risen in the settling vats. It is coagulated chemically and smoked in order to give it a hard cure, which ensures the greatest durability. The rubber required by this specification should be Hevea rubber of good quality, such as fine Para or smoked first latex.

Carbon is excluded because it is considered, by some purchasers, to be deleterious.

Red lead is excluded because of the possibilities of its deleterious effects on the rubber.

Ozokerite is prohibited because the acetone extract obtainable from it interferes with the separation of the acetone extract obtainable from the rubber, thereby vitiating the assay of the rubber extract. This prohibition is unimportant to the manufacturers, as ceresin, which is permitted, is the essential constituent of ozokerite.

An upper limit is placed upon the rubber in order to prevent the attainment of electrical and mechanical strength by the use of an extra quantity of inferior rubber whose lasting qualities might not be satisfactory.

The hydrocarbons are limited, owing to their tendency to separate from the compound and thus possibly cause porosity.

The free sulphur is limited because an excessive amount may be deleterious.

The maximum limit on the saponifiable acetone extract is to prevent the use of raw or reclaimed rubber with high saponifiable extract. The minimum assists in forcing the use of Hevea rubber, since it is characteristic of the acetone extract from Hevea rubber to be largely saponifiable.

The unsaponifiable resins are limited because a low proportion of unsaponifiable resins is characteristic of Hevea rubber. A high result might be due to the presence of reclaimed rubber.

The chloroform extract is limited, first to prevent the use of bituminous substances, and second, to limit de-polymerized and under-cured rubber.

The alcoholic potash extract is limited to prevent the use of saponifiable rubber substitutes.

The specific gravity is limited to reconcile the specifications of ingredients by weight with the practice of purchasing material by volume.

Fluorescence of the acetone solution is prohibited as it indicates the presence of mineral oils.

The color of the acetone extracts is specified to conform with the normal color of the extract from Hevea rubber. A darker color indicates adulteration or an inferior grade of rubber.

The hydrocarbons are required to be solid in order to prevent the use of oils and paraffin of low melting point. The shade required is that obtained from paraffin wax or ceresins. If hydrocarbons B are liquid this would indicate reclaimed rubber softened with mineral oil, or a poor grade of paraffin.

The color of the chloroform extract is specified to conform with the color of dissolved gum in minute quantities. The presence of bituminous substances would be indicated by a brown or black color.

It would be desirable that the sulphur of vulcanization be limited to exclude reclaimed rubber, which contains the sulphur of its previous vulcanization, but the committee has not yet developed an acceptable method for determining this quantity. It is therefore, confronted with the choice of either placing a limit on the total sulphur or giving up the attempt to exclude shoddy or sulphur limitations. Option is therefore given to the purchaser to insert or omit the limit on total sulphur. Such insertion will at times exclude reclaimed rubber and the committee believes it possible to make a suitable compound with this limitation. The committee thinks that a sulphur limit positively excluding reclaimed rubber, would place too great a hardship, in other ways, on the manufacturers. Where the specification is used with no total sulphur limit, the use of many kinds of, or much, reclaimed rubber, will be guarded against by the limits of the various components of the acetone extract. When the limitation on total sulphur is omitted, sulphur-bearing fillers, which possess certain advantages, may be used.

This specification should be supplemented by appropriate elasticity and tensile strength tests, in order to add to the assurance that good rubber has been used and that the vulcanization process has been properly carried out; also by appropriate electric stress and resistance tests, to assure proper insulating qualities and homogeneity of structure. The exact values of the limits for these tests will depend upon the use to which the material is to be put.

Navy Department specifications "51S6a," sal ammoniac, March 15, 1913, superseding part of "51S6," May 16, 1910, are as follows:

1. Sal Ammoniac for Galvanizing Purposes.—Must be of a good commercial grade of what is known as "gas-house" sal ammoniac and contain not less than 90 per cent of ammonium chloride (NH_4Cl). To be of such fineness that at least 75 per cent will be held on a sieve having 18 meshes per square inch and not more than 10 per cent will be held on a sieve having 4 meshes per square inch.

2. To be delivered in well-made wooden hogsheads containing about 1,200 pounds, unless otherwise specified. Containers to be marked with the name of the material, the name of the contractor, the net and gross weights, and the requisition or contract number under which delivery is made.

FIREBRICK FOR USE IN OIL GAS GENERATORS.*

The firebrick in an oil gas generator is subjected to somewhat harder usage than in water gas practice, on account of the higher heats of gas making and the greater changes of temperature during the run. Most authorities insist that a good firebrick should be more than 55 per cent silica and less than 5 per cent of iron, lime, magnesia, potassium and sodium combined. As will be seen from the analyses submitted, brick which have given perfect satisfaction show higher percentages of the latter materials, and I believe these specifications are somewhat too strict for brick for oil gas generators.

There are, however, a great many points to take into consideration besides the composition of the brick. A satisfactory firebrick must have a high fusing point, be of uniform composition, and regular shape. The high fusing point is necessary for it to withstand the heat with which it comes in contact. The uniform composition tends to give it strength, and the regular shape makes the labor of laying less and enables the mason to get tight joints and a consequent good job.

The question of high fusing point is directly obtained by the chemical composition of the brick, and in purchasing brick one is limited in this respect by the clays that are available in that particular vicinity. The freight on firebrick for a considerable distance is so high that it is seldom profitable to purchase firebrick at a very great distance from the point at which it is to be used. It should be noted, however, that an ultimate analysis is not at all an infallible guide as to the high fusing point; a mechanical analysis is a very great help. The condition of the silica content, whether as quartz, or combined with alumina, has a great bearing on the refractoriness. This point is fully covered by paper in the *Journal of Gas Lighting*, June 23d, 1908, by Mr. Frederick J. Bywater, Birmingham, England. I might say that this article by Mr. Bywater affords the most satisfactory information I have been able to find on the subject, and anyone interested could study it with great profit.

The uniform composition and regular shape of firebrick are strictly questions of manufacture, and this is a point which should be given very careful attention. There are tricks in all trades, and the firebrick manufacturer knows a number of them which he is unwilling to divulge. I have had no personal experience in the manufacture of firebrick from clay, but have had considerable experience in the manufacture of bricks and briquets from carbon, and while, of course, there are many points of difference, I can readily see that the question of tempering and mixing the material to be bricked, the pressure under which they are made, and even the design of the press, can have great bearing on the quality of the brick manufactured. The mate-

*Paper prepared by Mr. D. J. Young, for 20th Convention, Pacific Coast Gas Association.

rial to be bricked must be thoroughly mixed and tempered; that is, the moisture-content must be brought to a point so that the brick under pressure will bond itself satisfactorily and be of uniform strength. I know that, with a carbon, a difference of 2 per cent or 3 per cent in moisture will mean the difference between a substantial brick and one that will not stand handling. I might mention at this point that it is very easily possible to get a brick which is too dense, especially for checkerbrick, but as a denser brick weighs more, and as a consequence takes more material to make it, the brick manufacturer will generally see that it does not contain too much material. The use of grog or ground up firebrick, which has before been thoroughly burned out in use, is another point that calls for considerable experience. The grog is generally more nearly free from impurities than the original clay, and is mixed with the clay to bring up the percentage of silica and alumina. The burning of brick is largely dependent upon the judgment of the men in charge of the kilns, and it is very difficult to get information about temperatures and length of time they should be burned, as the manufacturers guard these facts as trade secrets. It is to be regretted that there is not more co-operation between the manufacturers and users of firebrick in this respect, which I am sure would result in great benefit to both.

In purchasing or receiving brick the purchaser should insist on all the brick being well burned. The outside should show a light brown color. If the bricks are burned at this temperature one can readily observe the quantity of impurities in the brick which will cause fluxing. I might mention at this point that it is comparatively a simple matter for the manufacturers to color a brick as it had been thoroughly burned. This is done while burning by the use of oil which has not been thoroughly consumed. However, a little experience will enable one to tell whether the brick has been colored by the use of oil or by the temperature of burning. I have had trouble a few times with a brick which we have designated a "puffed" brick. I do not know exactly how this occurs, but apparently is caused through the outside of the brick being burned very thoroughly without the heat penetrating to the center. Such a brick when broken shows a considerable difference in hardness between the outside and the inside. This brick when put in use seems to disintegrate very rapidly, and it should be watched for. It can frequently be determined by the checks in the face of the brick.

There is a considerable argument, even among the manufacturers, as to whether a wire cut or a repressed brick is the better. A wire cut brick has the four edges smooth from the pressure on the block from which it has been cut, and the sides are rough from being cut with small wires. The manufacturers of the wire cut brick claim that this brick is stronger than the repressed brick, the repressing destroying something of the bond of the brick. As to the merits of this claim I

do not know, but I have used the wire cut brick and the repressed brick with apparently the same results. One thing in favor of the repressed brick is that it is more likely to be uniform in size and have sharp edges allowing closer joints to be made.

Table I shows some analyses of various fireclays and bricks, both used and unused. The first nine samples were taken from "Engineering Chemistry," by Thomas B. Stillman. The other samples were analyzed by our chemist and are all from California clays:

TABLE I.

Sample No.	Silica.	Ferric oxide.	Alumina.	Titanic oxide.	Calcium oxide.	Magnesium oxide.	Potassium and sodium oxide.	Loss by ignition.	Total.
1 ...	50.46	1.50	35.90	...	0.13	0.02	...	12.74	100.75
2 ...	50.15	0.83	35.60	...	0.11	0.16	0.07	13.61	100.53
3 ...	56.42	1.33	26.35	1.15	0.60	0.55	0.48	13.75	100.63
4 ...	65.10	1.92	22.22	...	0.14	0.18	0.18	9.86	99.60
5 ...	44.84	0.46	36.30	...	0.19	0.19	0.42	17.78	100.18
6 ...	98.31	0.18	0.72	...	0.22	...	0.14	0.35	99.92
7 ...	45.48	0.90	38.54	...	0.08	0.38	0.66	13.00	99.04
8 ...	66.08	1.45	20.87	1.14	0.30	...	1.55	8.61	100.00
9 ...	44.40	0.45	39.14	1.05	...	...	0.25	14.95	100.24
10 ...	55.78	3.39	26.93	0.60	0.60	...	0.38	12.21	99.89
11 ...	57.94	2.40	24.36	1.20	2.06	...	1.32	11.20	100.48
12 ...	64.36	2.20	22.00	1.80	2.74	Trace	0.16	7.15	100.41
13 ...	71.42	3.20	16.56	...	...	...	3.82	5.42	100.42
14 ...	63.38	4.39	22.09	...	2.16	...	1.00	6.71	99.76
15 ...	70.84	3.99	20.21	0.80	3.74	...	0.82	...	100.40
16 ...	65.40	4.39	26.77	1.60	0.86	...	1.32	...	100.34
17 ...	68.08	3.79	24.31	0.60	2.34	...	1.26	...	100.38
18 ...	58.62	4.19	34.99	0.80	1.74	Trace	0.34	...	100.68
19 ...	69.32	4.19	22.85	0.80	1.70	Trace	0.50	...	99.36
20 ...	68.48	2.99	25.02	1.20	1.48	...	1.65	...	100.72
21 ...	66.70	4.59	25.60	1.40	1.32	Trace	...	...	99.70

Sample No.—

- 1—Mt. Savage fireclay, Md.
- 2—Fireclay, Clearfield Co., Pa.
- 3—Glenboig clay, England.
- 4—Stourbridge clay, England.
- 5—Saaran clay, Germany.
- 6—Dinas firebrick, England.
- 7—Zettlitz clay, Bohemia.
- 8—Stoneware clay, New Jersey.
- 9—Paper clay, New Jersey.
- 10 to 14—Various fireclays from Southern California.
- 15 to 18—Various firebrick from Southern California.
- 19 to 21—Various firebrick from Southern California after use.

I am of the opinion that the design of the generator and the workmanship on the brick of it have a great deal more to do with life of the firebrick than the quality thereof. Of course, if the brick will melt at the temperature to which it is subjected, it is impossible to work sufficiently good to make it stand up; but with the best brick it is easily possible, by faulty design of the brickwork, or poor workmanship, to have the brickwork give way in a very short time. We have found it profitable to have a special brick made to fit every condition that we will meet in bricking a generator, and these bricks are put in the generator with the use of very little fireclay. The clay is mixed in a thin mixture, the bricks are dipped in it and placed tight against each other. In work on our generators we never use a trowel. The bricks are forced in place by hammering and the joints made as noted above

by dipping. Where it is necessary to key an arch or circle, we have various sizes of key bricks, so that we can get one to fit without cutting a brick. The drawing, Fig. 1, shows the method of bricking a 20-inch shell. The lining and dome of this shell are practically two bricks thick, or 18 inches. As the generator is lined the surface of the lining and dome is painted with a mixture of fireclay and salt, using 5 per cent to 10 per cent salt. When the generator is heated up, this

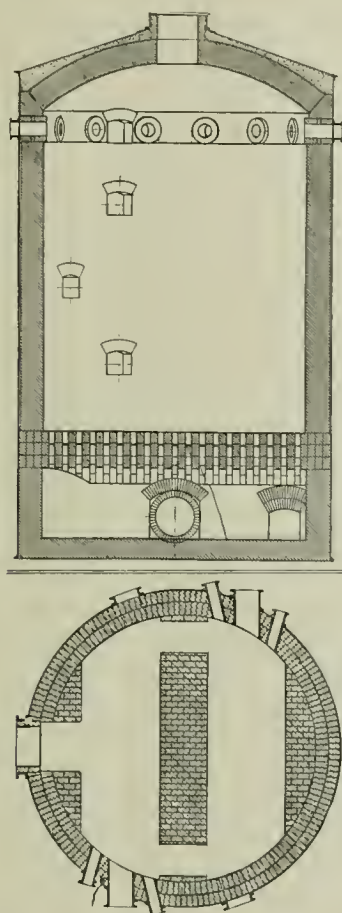


Fig. 1.

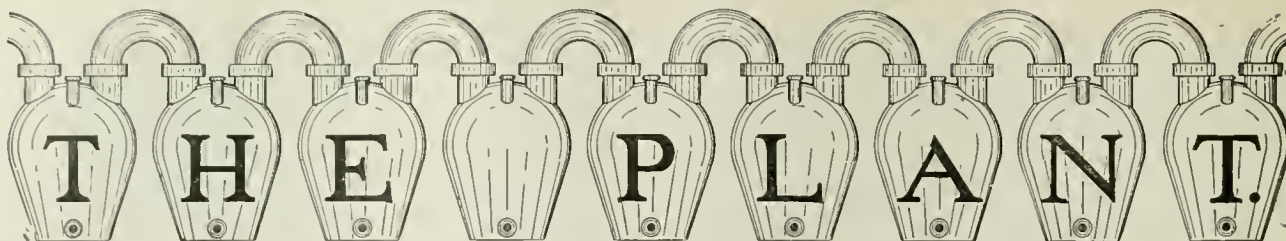
salt fluxes the clay and the surface of the dome, lining, arches, in fact of all the brickwork, except the checker-work, is covered with a thick glaze, making the lining present a surface practically the same as if it were made of one brick. This method is so successful that we have never had to remove the lining of a generator. The dome arch, which as you will note from the drawings is rather a large one, lasts for years. We have a dome of this type in constant use for 3 years, which on examination this summer appeared to be as good as when it was first built. This arch is made of brick as per sample No. 15. The failure of these arches is never from the melting of the brick, but is caused by the cutting action of the blast on the edge of the bull's-eye in the center. When these bull's-eye have failed, we noted that there was no sign of the brick melting, but it was evidently from the action of the blast. You will note from the design of the

firebox arches that these are made 3 brick thick, and we have never lost more than the bottom ring of this arch. This ring always appears to give down more from the action of the blast than from the melting of the brick. It is a very simple matter to put in the bottom ring of these arches without interfering with any of the brick above them, and they are then as good as new. We have been using this type of brick work for about 7 years.

There seems to be considerable difference of opinion as to whether brick should be put up in flues or staggered. We have experimented with both methods and have finally adopted the flue system of checkering the generator. It is probably a fact that, theoretically, this is less efficient, but, with staggered checkerbrick in the manufacture of oil gas, the tendency to stop up with carbon is so great that we find in the long run it is best to use the flues. These checkerbrick are set about $2\frac{1}{2}$ inches to 3 inches apart, and we get from 2 to 3 years' use out of them without renewal, and the failure is then caused, I believe, by the disintegration of the top rows of brick on account of the action of the steam on them. I might note that we have recently installed superheaters for superheating the steam used in injecting the oil. I believe the results from this will be much better. These superheaters are put in the off-take pipe of the generator, and as the steam is heated by the gas leaving the generator, consequently it is done without any fuel consumption. When we first experimented with these superheaters, we got the steam heated to such a degree that it fused a brass valve. We have since then cut down the size of these superheaters and we now get the steam heated to approximately 150° superheat.

The length of life of firebrick in the generator is, to a very great extent, dependent upon the judgment and intelligence of the operator. It would be a very easy matter, with a generator of the type described, to have the arches and checkerbrick melted down within a very few days with careless operation. We have adopted the plan of (when a generator is down for repairs) taking the men who operated it during the last year into the generator and showing the condition of the brick; and, where possible, we demonstrated to them the proper method of blasting in order to preserve the brickwork. Along this same line I am of the opinion that the operation of oil gas generators is a larger factor in efficiency than their design. There are few places, where the judgment of an operator is of such prime importance and I believe this point should be thoroughly recognized.

According to the 1907 census, bricks manufactured in the United Kingdom, totaled 5 billion, not including 968,000 tons of fire brick and 150,000 tons of tile brick. The total value of artificial stone, concrete blocks, etc., produced was \$1,500,000.



EUROPEAN AND AMERICAN SULPHITE PROCESSES.*

As the European market demands paper with a special elasticity and ability to stand strain, indicated by the terms of the order, it is of the utmost importance to manufacture an extra strong and long sulphite pulp which can be produced in greater strength by the Mitscherlich process than by any other.

Mitscherlich digesters are upright, having a capacity up to 300 cubic meters equal to 10,500 cubic feet. As a cubic meter generally gives a yield of 85 kg., the output of such a giant digester is 25 tons per cook. The cooking time generally lasts eighteen to forty hours, depending on the grade of pulp to be manufactured.

Mr. Schlick says he has seen such giant digesters installed in a modern Dutch mill and learned that a digester of $6\frac{1}{2}$ meters diameter, equal to 21 ft., by 41 meters high, equal to 46 feet, has lately been installed by a Bavarian concern. These large digesters have a double brick lining of approximately 6-inch thickness and are heated by means of copper coils, these being placed in the lower part of the digesters, where they are maintained in place by means of hard lead brackets.

The following figures are given on older cook in such a giant digester:

Time		Temperature	Pressure
3:15	night	36-30	0.8
7	day	74-71	3.0
10		96-90	3.3
11		100-93	"
1		102-94	"
3		113-108	"
5		115-113	"
7	night	119-119	"
9		120-121	"
11		125-120	"
1		125-119	"
3		120-120	2.8
5		128-120	2.4
7	day	ready	2.2

These digesters are washed twice with warm water, and are not blown out but emptied through the bottom cover. It is impossible to blow out these large digesters as the coils are covered with burned fibers which would spoil the cook if disintegrated. These digesters produce a better fiber for the following reasons, among others:

1. The acid is not diluted by condensed steam and is therefore of equal strength in all parts of the digester.

2. The acid is of considerably less strength than in the direct process, this being very advantageous to the fibers themselves at the beginning of the cook.

3. Splendid circulation.

4. Longer digesting process, depending on the use of the coils, preserves the natural length of the fibers and allows low steam pressure.

And the yield is larger per cord.

These digesters, however, require labor in emptying and a larger capital outlay. As already noted, these digesters produce a very strong fiber, which however, cannot be used for every grade of paper, though the modern pulpmakers are able to cook special pulp for greaseproof imitation parchment, etc. The writer saw, for instance, Mitscherlich pulp beaten up within $2\frac{1}{2}$ hours in European beating engines, into a high grade greaseproof paper. However, this pulp was especially cooked for the purpose, and beaten in beaters of modern European design.

The advantages of the direct cooked pulp are its softness, which makes the product especially suitable for high grade writing papers and the like, and its suitability for an easy bleaching pulp. In order to combine the advantages of the direct and indirect cooking process, most Scandinavian and European mills are cooking in recent years with direct and indirect steam up to a certain temperature— 108° C.—and finishing the cooking with the indirect system, or cook with both direct and indirect. This is justified as the liquor requires the most heat units in its temperature to the cooking temperature and no harm can be done to the Mitscherlich process itself in heating up with indirect and direct steam together if only the acid has the right strength at the beginning of the digesting. The cooking process is thus shortened considerably without interfering with the process. The Kellner direct cooking process lasts mostly only 10 to 15 hours—though Kellner distinctly made special claims for the manufacture of a short cooked pulp and a medium and long cooked pulp.

As already observed, the direct cooked pulp is soft and of excellent quality for writing and high grade printing papers. American manufacturers prefer to use the Kellner direct cooked pulp as a rule, while the European pulpmaker uses generally Mitscherlich (several large concerns cook also directly for their own use) and adds a certain proportion of a good waste paper, etc., thus obtaining the same results. Another help for the European papermaker is the superior beating engines used by him, in which the

*From Pulp and Paper Magazine.

fibers are carefully split and fibrilized, not shortened as in a jordan. In fact, if the beating surface of a beater is properly proportioned, a jordan engine is not required for most papers, it being only an additional beating surface.

The European papermaker is compelled to deliver his goods according to a classified and specified stress, measured in kilograms, which means, if the paper is to have a strength of 4 kilograms, that a sheet of a length of 4 kilograms must not break by its own weight under the mentioned lines. Special testing machines serve this purpose and register elasticity as well as strength in one operation. As it is of the utmost importance that special papers destined for important purposes, must be of enduring permanency, the American Government last year demanded a certain guarantee as regards strength. The bids, however, were not numerous. We should, however, be prepared to expect some day similar requests, as scientific books for instance, are expensive to print and should be preserved. Although the chemical and mechanical woodpulp industry has had an enormous development we cannot say that the lifetime of the paper has been lengthened against the paper "our parents used to make."

Acid making in Europe is done by the tank system as well as by the tower system.

The tank system Dr. Frank, for instance (similar to the Burgess type), is formed by three tanks, the tanks being placed so that one tank can be emptied by gravity into the next one. The SO_2 gases are pressed by compressors into the lower wooden tank. The SO_2 gases which are not absorbed then enter under pressure the second and thereafter the third tank. These tanks are fed with lime water and are provided with agitators. The upper one receives the fresh lime water, afterwards being emptied into the middle and then into the lower tank. The compressing of SO_2 gases in the lower tank takes place so long as the acid has the required strength. The lime water is prepared in a small chest provided with agitators. The SO_2 gases are generally produced in Europe in flat burners sometimes provided with water cooled chests, sometimes without. The capacity of a large water cooled flat burner is sufficient for a 20 to 25 tons unit (10 per cent sulphur consumption).

These burners are fed mostly by compressed air, and the burners have a compressed air inlet in front as well as on the back, in order to mix the burning sulphur thoroughly with air. The SO_2 gases pass a "sublimator" composed of a water cooled upright cylinder provided with a guide plate. In recent years gas washers have also been used successfully, these being placed behind the combustion chamber. The reclaiming of SO_2 gases is done by pressing the relief gases through coolers. The condensed strong liquid is directly mixed with the acid in the reservoirs. The relief gas line is connected also with the acid reservoirs, being made generally from concrete and placed under

ground. The acid is brought in these reservoirs to the strength required, thus enabling the pulpmaker to make slight changes in the strength of the acid, without disturbing the continuity of the operation of the acid plant.

In the newer European mills, however, the tower system is chiefly adopted, according to the Kellner system. In fact, the Kellner system is perfect nowadays and it would not be of interest to repeat what is already generally known about it. As generally known, the tower system with dolomite stone filling gives a much whiter pulp, and the cost of dolomite is lower than that of burned lime. The writer saw a very interesting arrangement several years ago in a small European sulphite mill, where sulphur burners were connected to towers without any blowers. The flat burner was placed in the story above the ground floor. As the SO_2 gases have a higher specific gravity than the air they sink through the cooler down to the gas inlet of the tower while the natural draft in the tower (in this case an open high Mitscherlich tower) created the air supply. This is, of course, more or less of historical interest as one would hardly use only one single and open tower except on relatively small capacity.

ALASKA'S COAL DEVELOPMENT RETARDED.

The development of the coal resources of Alaska, according to a statement in a report on the mineral resources of the United States issued by the United States Geological Survey, has been held back on account of the lack of legislation permitting the exploitation of the known extensive and valuable fields. In 1912 the commercial product of coal in Alaska amounted to only 355 tons. In addition 900 tons were mined under the direction of the Bureau of Mines for testing by the United States Navy. The imports of coal into Alaska amount to about 100,000 tons annually, but most of the transportation and manufacturing industries of the territory now depend on California oil for their fuel.

Practically all of the corkwood exported from Spain is from Seville district, whereas only about one-sixth of the cork waste is exported from here. The total value of the cork exports of Spain during 1912 was \$9,553,969, divided as follows: Corkwood, \$528,810; small squares, \$356,229; corks, \$7,864,299; other manufactures, \$49,783; cork waste, \$754,848.

About 5,500 tons of cork sawdust are used in Spain annually in packing fruits for shipment. Some 40,000 persons are employed in some manner in the cork industry in Spain, with an average wage of about \$0.67 per day.

RESEARCH AND ANALYSIS IN CHEMICAL MANUFACTURING.*

By W. C. FERGUSON.

The constant growth in efficiency in manufacturing chemistry is largely the result of organization that ensures the orderly use of every varied talent required, and occupying a very important place in such organization is the fullest use of a research staff and of analytical chemistry. When it is realized that these departments should investigate all new processes; constantly improve existing ones; correct and explain irregularities of current operations; invent new processes; determine the valuation and exact composition of all raw materials and finished products; fix yields, and control the different stages of many processes, etc., it becomes clear that if these constructive forces are to be used to the fullest it must be through the creation of an organization that will automatically cause every department in the organization to co-operate with the research and analytical branches. The methods described below are the result of the writer's many years' experience in charge of the research work of one of the largest chemical works in America, and also in charge of the largest electrolytic copper refinery in the same country.

RESEARCH DEPARTMENT.

This department should investigate irregularities in current manufacturing processes, seek constantly to improve existing methods, and carefully consider new methods as they arise. Its duties should comprise: Investigating cheaper raw materials, new uses for products manufactured, new products, increased yields, greater purity of products manufactured, utilization of wastes, more efficient structural materials and apparatus, etc.

Great care should be exercised in the selection of an efficient research staff, which should embody all the varied talent and knowledge required in a wide field. The collective talent of this department should embrace thorough scientific education, especially in the principles of physics and chemistry; the power to imagine new processes, or causes of various irregularities of current processes, combined with the ability to submit such ideas to the test of experimental proof; the habit of accurate observation and the skill to deduce from such observation the correct conclusion; and the quality of seeing right through all the unessentials to the one vital thing that counts. All of these qualities, together with a knowledge of manufacturing that will make all conform to practical conditions, are essential. The department should have a manager with office organization and a properly equipped laboratory, where work can be carried on in a large enough way to test practical difficulties

and costs. There should be a research committee, meeting regularly to consider and advise upon all important investigations. If experimental work be decided upon by this committee, then, if the subject is new, the journal and patent literature bearing upon it should be abstracted and experiments usually begun upon a very small scale.

Each investigation should be made by a specially selected man, and this man made responsible, but he should consult other members of the staff whose knowledge or skill would be helpful, and reports should be presented to the research committee so that it could advise when necessary. At the conclusion of each investigation a detailed report should be made to the department. Exact estimate of cost should be made of each investigation in order to know the profit or loss in each particular case and also to estimate the value of the department as a whole.

The organization of this department should include: (1) Systematic abstracting from patent specifications and journals bearing upon all subjects of interest; copies of these abstracts should go weekly to all who can use them, with instructions to study them carefully and to advise the department of any subjects that seem to warrant investigation. (2) Thorough abstracting from the literature in the case of new work undertaken, thus becoming familiar with all that has been published relating to the subject. (3) Systematic information should be constantly and promptly obtained of all records of imports and exports and duties on all finished products and raw materials that would interest the company in connection with its current business or as suggesting new articles of manufacture. (4) Pamphlets describing machinery, structural material, etc., are many years in advance of books upon identical subjects. A pamphlet library should be maintained in co-operation with the engineering department. (5) The superintendents should make monthly reports for the research department embodying all ideas of their own or their assistants that might in any way warrant investigation. (6) Members of the research staff should visit all possible outside manufacturing plants with the object of acquiring knowledge that could be applied by the company to its own processes or organization. (7) There should be, through proper connections, systematic prompt advices of all improvements in foreign practice that would be of value. (8) Salesmen should seek to understand the different processes and the various ways in which the company's products are used, and also know what substitutes are used for the company's products, and (9) certain research work might be undertaken by candidates for the degree of Ph.D. in universities, thus making these institutions take a co-operative part in developing practical questions being considered by manufacturers.

ANALYTICAL DEPARTMENT.

This department, under the chief chemist, should

*From a paper read before the 8th International Congress of Applied Chemistry.

control all work relating to sampling and analysis. Its duties should comprise the analysis and sampling of all raw materials and finished products as well as such analyses as are necessary in the intermediate steps of some processes in order to ensure proper control. It should furnish figures used to calculate yields and perform all the analytical work in connection with investigations. It should also do all analytical work that will aid the manufacturing, sales, purchasing, and construction departments, and co-operate with the sales department in investigating complaints. It should also pay strict attention to investigating and adopting better methods. If a company has more than one laboratory, uniform methods of sampling and analysis, approved by the chief chemist, should be used throughout. The various precautions to be observed should be specifically and prominently outlined at the end of each scheme, together with the experimental data and all equations involved proving its accuracy.

The staff of the head laboratory should be organized into an analytical council holding weekly meetings, discussing at alternate meetings the company's standard methods of analysis and abstracts of promising analytical methods of analysis from the current chemical literature. These abstracts should be incorporated in the minutes of the meetings. All investigation along analytical lines should be carefully written up, whether results are favorable or otherwise, and these reports sent to other laboratories of the company when desired. Any new methods suggested through the chemical literature or by any of the chemists should be tried and, where an improvement is found, incorporated in the standard methods.

The policy of the analytical department should be to give its members a broad acquaintance with all the work of the department by having a system of rotation, regularly changing the work of each so that, as far as possible, every man could take part in the great variety of the determinations made. This would have the further advantage of protecting the company from any constant error into which one man may fall; and as an added protection, all the work should be systematically and independently checked by more exact or by different methods than those in daily use. In order to estimate each man's capacity and to charge up the analytical work properly the following system should be used: An analytical order should be made for each sample which comes to the laboratory, and on the back of this order is recorded the amount of time spent by each chemist in making the analysis. When completed these orders should be filed under the various departments for which the work is done, and from them calculated a monthly statement of analytical charges, the material used being based upon the cost for the previous year.

The head laboratory and office should have an extensive library and subscribe to all important periodicals. All works laboratories should at least have standard works of reference.

The accuracy of balances and weights, of measuring apparatus, thermometers and hydrometers, should not be taken for granted, but proved to be accurate by comparison with standards of known accuracy as often as required. All standard solutions should be checked by the head of the laboratory or his first assistant, and all important determinations should be made in duplicate.

The forms of organization described above should never be allowed to fall into the rut of dull routine, but the personnel of the men engaged in this work maintained at the very highest standard, and all the necessary plans as described carried out with enthusiasm and thoroughness. The personal co-operation of the men of this department with members of other branches of the organization would prove an important aid in maintaining interest in the work, and be mutually educating.

GEOLOGISTS LEAVE GOVERNMENT SERVICE.

An efficiency limitation of quite a different type from that imposed by the inadequate and dangerous quarters occupied by the United States Geological Survey is presented, according to the annual report of the Director, recently made to Secretary Lane, in the restrictions placed in one way or another upon the selection of personnel. Under "lump-sum" appropriations there is a fair opportunity to obtain high-grade service in the scientific and technical positions, yet even here the restraining influence of precedent prevents attaching to the higher positions salaries that are more than a fraction of those which the well-trained specialists best fitted for these positions can obtain for similar work in the service of corporations. This condition has resulted in many of the members of the Geological Survey leaving Government service at the time when they have become most valuable as public servants. Thus in the four and one-half years ending January, 1913, the number of geologists who left the Government service for the primary purpose of bettering their financial condition was 41, and these men are known to have received salaries outside of the public service amounting to an average immediate advance of 140 per cent, or practically two and one-half times the salaries paid them by the Geological Survey.

The only optimistic view to take of this condition, whereby some of the better men are constantly resigning in every branch of the bureau, is to count this loss to the Survey as one measure of the educational contribution that the public service is making to the world's work.

NEW SOURCES OF SULPHUR IN THE SOUTH.*

The monopoly enjoyed by the Union Sulphur Co. of Louisiana, in the production of sulphur in the United States will, it is expected, be broken this year by the commencement of operations in Texas by the Freeport Sulphur Co., which is now erecting a plant on the Texas coast, as a result of two years of exploratory work started by the Brazos Syndicate. As already reported in previous publications the new syndicate backed by ample capital has acquired 10,000 acres of land at the mouth of the Brazos River, about 40 miles southwest of Galveston. The operations of this syndicate will be of much importance to Texas, but are of special interest to the mining world by reason of the development of the sulphur deposits in the Bryan Heights "dome," a low mound rising about 15 ft. above the level of the surrounding plain.

Bryan Heights is one of the characteristic "dome" formations of the Gulf Coastal Plain and is ideally situated for the economic production of sulphur, being only one-half mile from the gulf coast and within about $3\frac{1}{2}$ miles of the harbor of the Brazos River, where the commercial center of Freeport is to be established.

The sulphur is to be recovered by melting *in situ* with superheated water and pumping the molten sulphur to the surface with the Pohle air-lift system—approximately the process patented by Herman Frasch, though differing in the details of its application. The original Frasch patent relating to the melting of the sulphur underground expired in 1908. A number of later patents relating to certain details of operation were taken out and some of these are still in force. Success in the use of the hot-water process by another company will have an important bearing on the sulphur industry and will doubtless stimulate the early development of other dome formations of the Gulf Coastal Plain.

The Freeport Sulphur Co., is the outcome of two years' exploratory work, in which the syndicate managers state that over \$150,000 was spent. After the Bryan Heights deposit was decided upon, land was acquired for a distance of $7\frac{1}{2}$ miles on the west bank of the Brazos River, and the broader general plans of the syndicate were developed. These include the establishment of a port, railroad and steamship connections, the building of a bridge across the Brazos River, the laying out of the town of Freeport, the erecting of a 2,000-bbl. sugar refinery, establishing a national bank, stores, warehouses, etc., besides the sulphur operation above mentioned, which in itself is an enterprise of no small proportions when all the contingencies involved in production and marketing are fully considered.

Evidence that the syndicate is amply able to finance and manage these operations is afforded by a glance at

the important names included in the personnel of its members. Among those who joined the syndicate were the following well known New York men:

F. A. Vanderlip, James Stillman and Samuel McRoberts, of the National City Bank; E. P. Swenson, of S. M. Swenson & Sons; Sidell Tilghman, of Tilghman Bros.; the late Edwin Hawley; F. Q. Brown, of Redmond & Co.; R. T. Wilson; John Hays Hammond, and A. Chester Beatty. Messrs. Vanderlip, Swenson and Tilghman have acted as syndicate managers, disbursing all funds until the various subsidiary companies were formally organized and prepared to take charge of their respective operations.

Besides the townsite company, banking corporation, etc., a terminal company will be chartered that will give free access to any railroad as well as free dockage, thus making Freeport literally a free port. The terminal company will undertake such railroad construction as may be necessary for suitable connections, and a bridge is being built across the Brazos River to Velasco to connect with the Houston & Brazos Valley R. R., in which the syndicate has an interest. It will thus connect Freeport with Angleton, 18 miles distant on the Brownsville branch of the Frisco System, and with the International & Great Northern R. R. at Anchor, 22 miles from Freeport.

As may be gathered, the operations of the syndicate will have an important effect on the commercial development of this portion of Texas. Iron-ore deposits exist within 130 miles of Freeport, this distance being almost identical with the rail haul of Mesabi iron ores to Pittsburgh. It is understood that negotiations are now in progress for the early development of these deposits for which Freeport is expected to be the outlet. Harbor improvements were begun at the mouth of the Brazos River a number of years ago; jetties were built, but the Boston company interested in the development of the Brazos country was unable to carry out its project. By removing what silt has accumulated in the river channel, a good harbor can be immediately provided.

When the dome formations in the South were being drilled for oil, sulphur was encountered in a number of instances, but little attention was paid to this fact. Indeed, such deposits were of no commercial importance prior to the development of the Frasch process, and since Mr. Frasch's great success, the process has been protected by patents, none of which expired until 1908. There was consequently little inducement to determine whether any of the other sulphur occurrences were of economic importance.

Bryan Heights was drilled for oil by five different companies; about sixteen holes, most of them for oil, were put down by these companies. Some gas was encountered and a little oil, but neither in commercial quantities. Logs of these holes, however, show that sulphur was encountered practically in every instance. But a single diamond-drill core remained in evidence; consequently, when the deposit was being developed

*From a paper by Richard H. Vail in *The Engineering and Mining Journal*.

by the Brazos Syndicate, eleven new holes were drilled on the dome at various places. Ten of these holes were drilled with a core drill, giving cores that have indicated a tonnage of sulphur running into millions of tons; the exact tonnage that is commercially recoverable is difficult to estimate but it is apparent that there is in the Bryan Heights dome a sufficiently large deposit of sulphur to be made the basis of an important commercial operation. Indeed the conditions of operation are so favorable that should the company choose to do so, it could probably compete with importers of Spanish pyrites in the manufacture of sulphuric acid.

The company does not care to supply details of the results of drilling, other than to say that about 760 ft. of gravel, "gumbo" and cap-rock were encountered; then about 150 ft. of sulphur-bearing limestone, dolomite and gypsum; there were some beds of pure sulphur varying in thickness from a few inches to 7 ft.; the sulphur ceased at from 900 to 1,100 ft., being succeeded by pure gypsum and rock salt, to which no commercial importance is at present attached.

Owing to the concentration of sulphur operations into the hands of a few and the policy of secrecy that has been maintained, it has been necessary to draw from a number of outside sources for information required to round out certain details of the present situation in sulphur. Kirby Thomas, in an independent report on Bryan Heights property in 1910, gives the results of the earlier drilling, and of the No. 4 or "D" hole drilled by the Gulf Development Co., with a diamond drill. This single core may be higher or lower than the average, but as it was the most specific evidence available, it was carefully examined by Mr. Thomas, who reported as follows: "This core shows 174 ft. of sulphur formation, of which 35 ft. is limestone and gypsum, showing sulphur estimated at less than 10 per cent; and 85 ft. of gypsum and limestone with 10 to 50 per cent of sulphur; 54 ft. of the core is missing, which indicates that the soft friable sulphur and gypsum in this much of the hole did not core. I examined all the 120 ft. of core inch by inch and made a sight estimate by bulk that more than one-third would run 20 per cent or better, and that about 50 ft. would run 10 per cent or better; about 20 ft. was barren limestone or gypsum."

The first unit of a plant to have a capacity of 120,000 tons annually was designed and is now being constructed by Westinghouse, Church, Kerr & Co., of New York, under the direction of Cloyd M. Chapman, engineer in charge, and Homer Burns, superintendent of construction. The new plant will have four 750-hp. Stirling water-tube boilers which will be operated at 100 per cent overload, delivering steam at 100-lb. pressure to three Blake jet-type marine heaters where the water that is to be pumped underground to melt the sulphur, will be heated to about 330° F. The large supply of water necessary for regular opera-

tion, approximating 2,400,000 gal. per day, will be pumped by 13 Platt Iron Works pumps. Six water wells have been driven on the flat outside of the sulphur area and other wells are being sunk to augment the present supply of water. For compressed air, there will be two Ingersoll-Rand compressors, one operating at from 350- to 700-lb. pressure and the other at 100-lb. pressure. The latter machine is to supply air for pumping water from the wells on the flat. Fuel oil will be used under the boilers and it is expected that about 900 bbls. of Tampico oil per day will be burned at the present plant. The company has erected at the mouth of the Brazos River a 55,000-bbl. steel tank, from which a 4-in. pipe line leads to the steaming plant. Affiliated interests of the Freeport Sulphur Co. own oil properties in Mexico and can deliver oil at Freeport under a very small freight charge.

The Freeport Sulphur Co. expected to begin the production of sulphur early in the autumn. Benjamin Andrews will be chief engineer and the drilling of the sulphur wells will be under the direction of A. Weber; both were formerly connected with the operations at Sulphur, La. The Bryan Heights products will be taken by rail to the Freeport dock. An affiliated steamship line is to be established and in this way the company will be able to make satisfactory delivery of its product to Eastern ports.

The sulphur industry in this country really began with the epoch-making process invented by Herman Frasch, for which in 1911 he was awarded the Perkin medal. This invention made possible the utilization of the deep-lying sulphur deposits of the Gulf Coastal Plain. Other sulphur deposits of the United States, such as are operated in a small way in Wyoming, Nevada and Utah, are disadvantageously situated with respect to transportation of products to other than local consuming centers. The sulphur production of the United States remained insignificant until 1903, when the Union Sulphur Co., succeeded in placing its operation in Calcasieu parish, Louisiana, on a commercial basis, producing during the year about 35,000 tons of sulphur. Since 1904, the commercial requirements of the United States have practically been met by the Union Sulphur Co., 90 per cent of the stock of which is controlled by Herman Frasch, the estates of H. McK. Twombly, Abram S. Hewitt, W. H. Tiers and Edward Cooper and H. L. Severence.

The cost of producing sulphur in Louisiana by the Frasch method is currently reported to be about \$5 per ton at the mine. Kirby Thomas in discussing this subject in the report referred to above says: "The court records in the Louisiana State Tax case against the Union Sulphur Co., show that up to the middle of 1907, the profits of the company had been \$4,545,077, on a production of 561,014 tons, including the small output of the earlier years when the process was being perfected. The selling price in New York has been maintained at about \$22 per ton for some time. The mine

cost of production at Sulphur, La., is reported to be about \$3 per ton, but from various data it is apparently in excess of this amount, perhaps \$6 per ton. The large operating expense is for fuel to heat the water introduced in the wells to melt the sulphur. The cost of installing a well was given in the Louisiana State case as \$7.102 and the daily cost of 'steaming' \$565; the average daily yield was reported at 203 tons and the average yield per well 8,363 tons. The Sicilian mines have a higher cost equivalent to about \$16 per ton, New York, as the conditions of operation are less favorable."

The growth of the sulphur industry in the United States is well presented in the accompanying statistics, taken from reports of the U. S. Geological Survey, showing the production of sulphur and also that of pyrites with which it is somewhat in competition in connection with the production of sulphuric acid. The statistics of the production of sulphur prior to 1904 are confused by the fact that sulphur and pyrites were reported together, the sulphur production being small at that period. The column showing the sulphur imports gives a better idea of the steady decline of the Sicilian predominance of the American market. The exports of sulphur from the United States amounted last year to over 28,000 tons, so that the United States may be said to be producing all the sulphur that it at present consumes in this form.

It will be noted, however, from the tables showing the production and importation of pyrites that this country still imports a large proportion of raw materials used in the production of sulphuric acid. Pyrites is used almost exclusively for the purpose of manufacturing sulphuric acid and only about 300,000 tons are mined in this country, while over 1,000,000 tons are imported. The sulphur content of the imported pyrites is equivalent to about 400,000 tons, from which it will be seen that there might be a large field for the utilization of American sulphur should the conditions of production and transportation permit it to be sold in competition with pyrites, the price for which ranges from about 10 to 13c per unit of sulphur.

Sulphur can undoubtedly be produced from favorably situated dome deposits using the Frasch process at prices ranging from \$5 to \$10 per ton delivered at the seaboard. This country has been consuming the equivalent of about 750,000 tons of sulphur annually.

Should the market for sulphur—which is principally used in the papermaking, bleaching, sulphuric acid and powder industries and in agriculture—fail to expand with the new production, an effort will doubtless be made to invade the acid-making field, now largely held by pyrites especially where great purity is not required.

The chief use of sulphuric acid in this country is in the manufacture of acid phosphate for fertilizer. For the making of the acid, the pure sulphur would have decided advantages over either pyrites or acid in freight charges to interior points. Thus, one ton of

pure sulphur would make about 3 tons of pure acid, while one ton of pyrites will make only about 1.4 tons

CONSUMPTION OF SULPHUR IN THE UNITED STATES. SULPHUR AND PYRITES IN THE UNITED STATES.

(Long Tons.)			
Domestic sulphur and sulphur content of pyrites.....			
469,613	350,494	362,703	
Imported sulphur			
21,136	30,589	30,833	
Sulphur content of imported pyrites (c)			
300,653	309,979	361,598	
Total domestic consumption....	791,402	691,062	755,134

(c) Based on average sulphur content of 45 per cent.

of pure acid; in terms of 50° H₂HO₄, the relative figures are about 4.8:2.3. The acid field would not be conquered in a day, however, as there are existing contracts and investments in pyrites-burning equipments that must be considered. Besides the natural inertia of the industry, there is likely to be hesitancy about installing any new equipment in this field until the possibilities of the Newberry-Fishburne calcining process—converting phosphate rock into citrate-soluble phosphate by calcination with lime or an alkaline salt—have been fully determined.

SULPHUR AND PYRITES IN THE UNITED STATES.

—Sulphur—			—Pyrites—		
Pro-duction, long tons.			Pro-duction, long tons.		
Year—			Year—		
1900....	3,147	167,696	1900....	204,615	322,484
1901.... (a)	241,691	175,210	1901.... (b)	241,691	403,706
1902.... (a)	207,874	174,939	1902.... (b)	207,874	440,363
1903.... (a)	233,127	191,032	1903.... (b)	233,127	420,410
1904....	127,292	129,532	1904....	207,081	422,720
1905....	181,677	84,339	1905....	253,000	511,946
1906....	204,153	74,241	1906....	261,422	598,078
1907....	293,106	22,523	1907....	247,387	627,985
1908....	369,444	21,136	1908....	222,598	668,117
1909....	239,312	30,589	1909....	247,070	688,843
1910....	255,534	30,833	1910....	241,612	803,551
1911....	265,664	29,144	1911....	299,904	1,066,310

(a) Includes the production of pyrites.

(b) Includes the production of sulphur.

The principal sulphur producing countries of the world are, in the order of their production: Italy (Sicily), United States and Japan. Sulphur is produced in a smaller way by a number of other countries, but these operations are not of international importance. There are, however, important known deposits in various places, such as in Northern Africa, the Caucasus and Transcaspian Territory, Mexico, Chile, and in a number of islands of the Pacific Ocean.

In 1865, while boring for petroleum in Louisiana, a deposit of sulphur was discovered at a depth of about 500 ft. An Austrian, a French and several American companies each attempted to sink a shaft through the overlying gumbo and quicksand, but without success and with some loss of life, due to inrushing water charged with hydrogen sulphide. Finally, in 1890, Herman Frasch, at that time a process expert for the Standard Oil Co., applied his genius to this problem. He concluded that the sulphur could be melted *in situ* with superheated water and pumped to the surface

while in molten condition. After many difficulties Mr. Frasch succeeded in putting his method in operation on a large and deservedly profitable scale. The working costs are the lowest obtained anywhere in the world, with the possible exception of the practically pure volcanic deposits, such as are mined in Japan. The latter, however, are handicapped by the high cost of transport to market.

At the presentation of the Perkin medal to Mr. Frasch, some interesting facts regarding the operation near Sulphur, La., were authoritatively announced for the first time by Mr. Frasch and other officials of the Union Sulphur Co. In view of the interest now being taken in sulphur production, it seems worth while to review some of the principal features of the Louisiana operation. At the time Mr. Frasch undertook the development of the Louisiana deposit, the dome formations of the Gulf Coastal Plain were little understood. In view of information received from the various companies, he believed that sulphur could be found anywhere in reasonable proximity to Sulphur Mine, where the land was still held at a high price in spite of the repeated failures. Accordingly he purchased land about $1\frac{1}{2}$ miles from Sulphur Mine and drilled a well 2,000 ft. deep without finding anything. Four wells were drilled before he reached the conclusion that the sulphur was all within the area then owned by a New York company, which was by this time glad to part with its property.

The sulphur-bearing area is nearly circular in shape and comprises about 52 acres. The wells are sunk in groups, the individual wells being placed 50 to 100 ft. apart. In the wells, a 10-in. pipe is sunk to a depth of approximately 500 ft. According to report, this hole is continued to a depth of about 630 ft., with a $9\frac{7}{8}$ in. drill and an 8-in. perforated liner is inserted to the bottom of the hole. Then a 6-in. pipe, reduced to 5 in. through the liner and perforated at the bottom, is inserted. A 3-in. pipe, also perforated at the base, is then run to the bottom of the 6-in., and a 1-in. pipe to the bottom of a 3-in. Water superheated to 335° F. is then pumped down the outer two annular openings and after two or three days sulphur is raised through the 3-in. pipe by means of compressed air from the 1-in. pipe.

The molten sulphur is raised to a height of about 70 ft. above the surface and delivered into plank bins about 65 ft. high and usually 150 ft. wide and often 250 ft. long. Blocks of sulphur have thus been formed containing 150,000 tons. The sulphur as it comes from the wells is over $99\frac{1}{2}$ per cent pure. The output of the wells varies from 200 to 500 tons of sulphur per day, and, in one case, a single well produced over 73,000 tons. When it is desired to ship the sulphur, the planking of the bins is removed and the sulphur is blasted and loaded into cars by locomotive cranes fitted with 2-ton grab buckets. It is then sent by rail to Sabine, Tex., where dock-loading facilities permit the loading of a 7,500-ton steamer in 12 hours.

Owing to the porous nature of the sulphur-bearing

rock, an enormous volume of water is required for melting the sulphur. The average daily consumption of water is about 7,000,000 gal., which is obtained from a pumping station on the Houston River, about six miles from the mine. The Union Sulphur Co. has about 130 boilers arranged in eight batteries, representing a total boiler capacity of about 25,000 hp. One of the interesting features of this large power equipment is that but a small proportion of the steam generated is used for power.

The fuel consumption amounts to about 700 bbl. of oil per day at each battery, and the average yearly consumption is over 1,000,000 bbl. In the rear of each battery are the pumps and superheaters. The latter are vertical, cylindrical receptacles, about 4 ft. in diameter and 16 ft. high, containing a series of shallow trays.

When the first sulphur was melted by Mr. Frasch's process, an ordinary deep-well pump was used for bringing the molten sulphur to the surface. Much difficulty was experienced with the valves, on account of the high specific gravity of the sulphur and the corrosive action of the mineral itself. Zinc and aluminum, the only two metals not seriously corroded by liquid sulphur, proved too soft to resist the shock of the pump stroke and it was not until compressed air was successfully applied to this part of the operation that Mr. Frasch felt that commercial success had been achieved.

Other unforeseen difficulties arose. Wells were lost by the parting of the pipes. As the sulphur melted out, the rocks and overlying sands would settle, the grip of the sand and earth pulling the pipe in two and the well would be lost. A 12-in. pipe, telescoping the 10-in. pipe obviated this difficulty. The life of wells was also increased by lining the hole drilled through the rock with an 8-in. perforated pipe. All wells, however, are eventually lost by caving.

Wild, cold water caused some wells to cease producing. This was first obviated by pumping in sawdust with the melting water. After pumping in about 30 cars of sawdust, one well again began producing and 39,000 tons more of sulphur was obtained before caving of the rock broke the pipes. This idea was expanded in several ways. Whenever a well breaks, the company dynamites the 10-in. pipe in the quicksand above the rock; the sand follows into the cavity and fills the space formerly occupied by the abstracted sulphur. In time, the clay of the surface slowly drops into the place of the quicksand, and, in some cases, the subsidence has amounted to 80 ft. In order to maintain the pressure necessary to prevent the superheated water from breaking into steam, the volume of sulphur extracted below must be replaced by earth. To do this a dredge with a capacity of 4,000 cu. yd. per day became necessary, and its operations have resulted in numerous reservoirs on the outskirts of the property.

In Sicily, which is still the most important producer of sulphur, the industry through over-production got

into such a demoralized condition that six years ago it was made a government monopoly. The entire output must now be sold to the *Consortio Obbligatorio per l'Industria Zolnifera Siciliana*. The statistics of production for the year ended July 31, 1911, as recently reported,¹ were as follows: Total production, 391,978 metric tons; exports, 456,227; stocks on hand, 534,603 (a decrease of 61,525 tons); buying price, \$17,466 per metric ton; selling price, \$18,225; average cost of raw sulphur at the mines, \$10.61; transport to point of shipment, \$0.96; warehousing and loading, \$0.96 per ton.

The sulphur in Sicily is found chiefly in an argillaceous limestone, associated with gypsum and bituminous marl. The sulphur-bearing rocks occur in the form of immense lenses rather than as extensive beds, as this term is commonly understood. There are usually three or four layers of sulphur-bearing material of variable thickness and width. The richer deposits carry from 15 to 20 per cent sulphur, but occasionally individual deposits are known to have 50 per cent or even up to 80 per cent or 90 per cent of sulphur. Ore carrying less than 8 per cent is not considered workable. The ore is mined in a primitive manner and is treated in a variety of ways, the greater amount being treated either in ovens or the so-called *calceroni*; and a smaller amount is melted out of the ore by means of superheated steam; some ore is roasted in heaps, and the sulphur which accumulates at the bottom is collected in shallow pools. This method, however, recovers only about 33 per cent of the sulphur in the ore. The cell oven is superseding the other methods, though the use of superheated steam is also growing.

The so-called "domes" of the Gulf Coastal Plain occur in a region that is monotonous topographically and stratigraphically. The irregularities in the contour of the surface are often discernible with difficulty; some of the domes are represented by low mounds not exceeding 10 ft. in height and they are of limited area, say from 200 to 2,000 acres. The rocks of the region are Cretaceous, Tertiary and Quaternary sediments which, west of the Mississippi, dip gently in a southeasterly direction. Local uplifts occur, the structure of which is well presented in descriptive illustrations by Prof. G. D. Harris who has given these structures much study and from whose writings quotation has been freely made. These remarkable uplifts have been styled "domes" but this term refers to the structural rather than to the topographic feature: the newer domes along the gulf border are really domes topographically as well as structurally, but the older domes to the north are apt to be topographically plane, or even concave. It was a number of years before the existence of these quaquaversal uplifts was recognized, and their full commercial importance was not realized until Capt. A. F. Lucas who had been exploring the salt deposits of Louisiana became convinced that such domes might also contain commercial deposits of sul-

phur and petroleum. His theory was proved in a spectacular manner in 1901 at the Spindle Top dome where a great gusher was brought in as a result of drilling he had inaugurated. Those who disregarded this theory and drilled outside the dome failed to find the "lateral extension of this oil field," as Mr. Frasch had failed to find the extension of the sulphur-bearing area when he sunk wells $1\frac{1}{2}$ miles from Sulphur Mine.

The origin of the domes was a subject of much discussion by geologists and engineers who were at work in the South, prominent among whom were Hilgard, Lerch, Lucas, Veatch, Hill, Heyes, Kennedy, Hager and Harris. In his 1907 report to the Geological Survey of Louisiana and in a more recent contribution to *Economic Geology*, Harris discussed these structures at length. The domes are considered as having formed: (1) By precipitation due to decrease in temperature; (2) by lifting the overlying rock and earth by the power of growing crystallization. On the latter point, it may be remarked, there is not complete agreement.

CHINESE VEGETABLE OILS.

Consul General George E. Anderson, Hongkong, reports that in spite of many drawbacks there has been a steady increase in the export of vegetable oils from China during the last four years. Heretofore the increase has been largely in soya-bean oil from North China, but the increase in 1912 was experienced in spite of a serious falling off in the volume and value of exports of bean oil. There were increased exports of peanut oil and of wood, tea-seed, and other vegetable oils. The exports for 1911 and 1912 are shown in the following table:

Oils—	—1911—		—1912—	
	Net tons.	Value.	Net tons.	Value.
Bean	47,503	\$3,792,341	35,046	\$2,922,872
Peanut	17,386	1,644,035	20,281	2,628,531
Wood, tea-seed, and other vegetable	37,089	3,516,713	44,815	4,916,878
Total	101,978	\$8,953,089	100,142	\$10,468,281

The decrease in the export of bean oil was caused by the high price of beans in China at a time when oil-bearing seeds in Europe were unusually plentiful and cheap. The course of the market last year has done much to dispel the boom ideas generally entertained as to the future of the product in North China. Nevertheless, the trade on the whole has shown great development, and recovery in the bean trade may be expected at any time. The exports of these oils in 1910 amounted to 95,825 net tons, valued at \$8,720,438. In 1909 and previous years the exports of such oils were valued at an average of only about \$3,500,000 gold annually.

The exports of these oils for the present year (1913) have not been so satisfactory. The declared exports of peanut oil from Hongkong, which usually handles about 60 per cent of the exports of oil from China to the United States, have fallen off about 50 per cent during the 9 months ended with September as compared with the corresponding period of 1912.

¹ Daily Consular and Trade Reports, Aug. 21, 1912.

² Die wichtigsten Lagerstaetten der Nicht-Erze, by O. Stutzer; Borntraeger Bros., Berlin, 1911.



METHODS OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR INSTITUTE OF TECHNOLOGY.

The Analysis of a Sample of Monel Metal.

In the course of preparing and analyzing a series of alloys for the use of students of analytical chemistry, the writer examined a sample of Monel metal. As the particular combination of metals in that interesting substance is rather out of the ordinary, the method used is here described, in the hope that it may be useful.

Monel metal is described in a circular of the company producing it as having the following composition:

Nickel	67.00%
Copper	27.00%
Other metals (iron and manganese)	6.00%
	100.00%

For the analysis, half gram samples of fine chips were taken.

The sample is dissolved in as little dilute nitric acid as possible, and after complete solution, about 5 c.c. of concentrated sulphuric acid added and the whole evaporated to copious fumes of sulphur trioxide. After cooling the sulphates are taken up in water, the solution being diluted to about 100 c.c. To this about 50 c.c. of strong sulphurous acid solution is added, the whole heated and about 2 gms. of KI dissolved in a few c.c. of water added. The whole is boiled for a few moments, when the white precipitate of CuI should settle readily, and appear almost like a precipitate of AgCl. The solution should smell strongly of sulphur dioxide throughout the operation. The CuI, which should be perfectly white, is thrown upon a Gooch filter which was prepared in the usual manner, washed with alcohol, then ether, and, after heating for 20 minutes at 105° C., weighed. The CuI is washed several times with dilute H₂SO₄, that solution being employed in transferring the precipitate from the beaker, then washed with a little alcohol, then with ether, and finally dried at 105° C., for 20 minutes, and weighed.

$$\text{Weight of CuI} \times 0.3339 = \text{wt. Cu.}$$

W. Cu.

$$\text{————} \times 100 = \% \text{ Cu.}$$

0.5

The filtrate from the copper is boiled thoroughly to remove all SO₂ and to concentrate it. To the hot solution is added about a gram of ammonium persulphate, and then, slowly, dilute ammonia solution to alkalinity. The precipitate of ferric and manganese

hydroxides is filtered off on a small paper, washed once with hot water then is dissolved in hot dilute hydrochloric acid into a smaller beaker and reprecipitated by ammonia and ammonium persulphate, the filtrate being added to the previous filtrate. The precipitate is burned in a platinum crucible, blasted, and weighed as Fe₂O₃ + Mn₂O₄. It is then fused with KHSO₄, the fusion extracted with water and dilute sulphuric acid, the ferric sulphate reduced by means of iron-free, amalgamated zinc, and titrated in the cold with standard permanganate solution.

$$\text{C. C. KMnO}_4 \text{ sol.} \times \text{st'd}$$

$$\text{————} \times 100 = \% \text{ Fe}$$

0.5

$$\text{wt. Fe} \times 1.4300$$

$$= \text{wt. Fe}_2\text{O}_3$$

$$\text{wt. precipitate (Fe}_2\text{O}_3 + \text{Mn}_2\text{O}_4) - \text{Fe}_2\text{O}_3$$

$$= \text{wt. Mn}_2\text{O}_4$$

$$\text{Mn}_2\text{O}_4 \times 0.7202$$

$$= \text{wt. Mn}$$

$$\text{wt. Mn}$$

$$\text{————} \times 100$$

$$= \% \text{ Mn.}$$

.5

The combined filtrates from the iron and manganese contain all the nickel which is to be determined by the well known dimethylglyoxime method. Inasmuch as the precipitate formed by this reagent is very bulky, the weight of nickel precipitated should not be more than 0.1 gm., for the sake of convenience in handling the precipitate. To this end the combined filtrates from the double precipitation of iron and manganese, after acidification with dilute hydrochloric acid, are made up to 1,000 c.c. in a standard measuring flask, and 250 c.c. taken for each determination, care being taken that the temperature be constant. The acid solution, which represents one-fourth of the sample, is treated with an excess of a six per cent solution of dimethylglyoxime in absolute alcohol, and the whole raised to boiling. Ammonia is then added, with stirring, until the solution is just alkaline, the brilliant red precipitate of the nickel derivative of dimethylglyoxime appearing. The solution should be boiled a few moments, and a few drops of precipitant added to make sure of complete precipitation, when the precipitate is filtered out upon an 11 cm. *hardened* filter, and washed thoroughly with hot water. The precipitate prepared under these conditions filters and washes readily. It is now transferred by the aid of a very fine stream of water from the wash bottle, from the paper to a weighed platinum dish (the precipitate washing off the hardened paper very readily and completely) and the dish and contents placed on the water bath and heated to dryness. Drying is completed in the air bath at 100° to 105° C., and the whole weighed.

This gives the weight of the precipitate $(C_4H_7N_2O_2)_2Ni$, which contains 20.31% Ni.

$$\frac{Wt. (C_4H_7N_2O_2)_2Ni \times 0.2031 \times 4}{0.5} \times 100 = \% Ni$$

The results of the writer's analysis, made rapidly, and without any great effort to achieve extreme accuracy, follow:

Ni	= 26.95%
Fe	= 3.00%
Mn	= 2.95%
Ni	= 66.94%
Total	99.84%

TESTS FOR DETERMINING QUALITY OF PAPER.*

By K. B. LAMB, CH. E.

A good deal of interest in paper testing has been shown lately by those who use, buy, sell or manufacture paper in quantities, and it is the purpose of this article to explain in a comprehensive manner just what tests are made in the paper testing laboratory, and the commercial value of such tests.

Paper testing is of course primarily of value to the consumer, who is to be found in practically every line of business. Often large sums of money are spent on the item of paper alone, but as a rule the consumer has no way of judging the character or quality of the paper or its suitability to his particular needs, except through observation or the word of the salesman who is selling it to him, and who is, of course, chiefly concerned in making a sale.

That observation counts for a great deal in determining the suitability of a paper and in the estimation of widely different types cannot be gainsaid, but can observation tell which of two writing papers is the better? They may look and feel much alike and yet be widely different in quality and have many different properties. Mere observation cannot answer questions such as these: How much rag stock is there present? How much woodpulp? How much mechanical pulp and how much chemical pulp? What is the weight per ream, what is the strength, and the strength in comparison to the weight? What is the folding endurance? What sizing materials are used and how much? What is the proportion of loading materials present, etc.

The answers to questions like the foregoing, while not meaning much to one who knows little about paper constitute the basis for determination of questions such as the following: Will the paper in question stay white or turn yellow with age? Will it take ink well? Is it strong enough for the purpose to which it is to be put, and will it endure folding? Will it emboss well? How many sheets are there to the pound?

Are you paying for paper or excess mineral loading? Will it expand little or much under diverse atmospheric conditions?

Another and probably the most important use to which accurate paper testing can be put is in relation to buying on specification. If he is wise the consumer will make the firms selling him the particular kind of paper he wishes submit samples and estimates. He will then have a chance to compare the kinds and qualities of paper on the market and the prices of the different firms. He gets a greater variety to choose from, and also, by letting it be known that the samples are submitted on specification, he gets the best price possible for the given quality of goods. Paper testing here performs the duty of determining which sample represents the best value for the money.

In controlling shipments paper testing is also of value as it shows whether the paper is up to specification and whether the consumer is getting what he contracted for. The United States Government a few years ago undertook to control all the paper used in the different departments by buying on specification and by testing shipments and was in many cases actually able to get a better paper at a cheaper price.

In view of the foregoing it may be stated that paper testing in general is of use:

(1) In determining the best value obtained from money paid; (2) in buying on specification, determining which paper submitted is most suitable and economical; (3) in insuring uniform deliveries and maintenance of quality.

The tests naturally divide themselves into three divisions with subdivisions as follows:

(1) Microscopical tests—

- (a) For character of fiber.
- (b) For proportion of each constituent.
- (c) For quality of fiber and pulp.
- (d) For character of process used to manufacture pulp.

(2) Physical tests—

- (a) Bursting strength.
- (b) Tensile strength.
- (c) Thickness.
- (d) Folding endurance.
- (e) Weight per ream.
- (f) Absorption.
- (g) Expansion.

(3) Chemical tests—

- (a) Percentage of ash.
- (b) Percentage of rosin size.
- (c) Percentage of animal size.
- (d) Qualitative tests for starch, acid, sulphur, chlorine, glue, loading materials, coloring matters, etc.

I. MICROSCOPICAL TESTS.

The microscopical examination is the most important of all as it shows what stock has been used in making the paper. It shows the character of the fibers used, both through their physical appearance and the

*From Paper.

colors taken by them with various stains. The proportion of each constituent can be estimated within 5 per cent and the quality of pulp and nature of beating is easily discernible to the practiced eye. The character of the process used to manufacture the pulp can also be determined both by the appearance of the fibers, which in the case of mechanical pulp are much torn and mutilated, and by color reactions with different stains, "Herzberg's stain," for instance, giving a blue color with chemical woodpulp, a yellow color with mechanical woodpulp and a wine red color with rag stock.

Briefly the method of preparation for microscopical analysis is as follows. Small representative samples of the paper are boiled with 0.5 per cent sodium hydroxide solution. This removes everything but the pulp which is broken up on shaking in a test tube with a little water. Some of this pulp is next transferred to a microscope slide with a dissecting needle, the excess water removed, and a drop of the stain added. A cover glass is now placed on top of the fibers and they are ready for examination.

II. PHYSICAL TESTS.

The physical tests are also very important as they determine strength, weight, etc.

The bursting strength is found by clamping a sample of the paper in a machine over a rubber diaphragm which is expanded upward by glycerin forced from a reservoir by means of a screw feed, a gauge attached to the reservoir giving the pressure in pounds per square inch. By use of the rubber diaphragm a uniform pressure is obtained. The tensile strength is obtained by clamping a strip of paper in a machine which exerts a uniform and regular pull until the sample breaks, the breaking point and also the elongation being carefully noted. Both tests give the strength of the paper and are particularly useful in testing wrapping paper where strength is an important factor.

The determination of thickness is effected by means of a micrometer gauge. This gauge is provided with a spring which presses the plunger rod on the paper, thus providing a uniform pressure in every case. The thickness is read on a dial above in thousandths of an inch, it being possible to estimate to ten thousandths. This, combined with the bursting strength or tensile strength of the paper, gives the relative strength. Folding endurance is found by means of a machine in which a strip of the paper is clamped under a uniform tension and which folds the piece of paper back and forth until the latter breaks, the number of such folds being automatically recorded. This is a very useful test for papers which are subjecting to much wear and tear. Weight per ream is obtained by weighing several representative sheets and calculating the total weight. Absorption is mainly used to test the quality of blotting papers and is carried out by allowing strips of the paper of uniform width to

dip into a beaker of colored water, and finding how high the water rises in a given time.

III. CHEMICAL TESTS.

Chemical tests are of use in showing the quality of the paper in those ways in which it is dependent upon the character, quality, and amount of materials used in its manufacture, aside from the pulp. They determine whether the paper is unduly loaded, whether it will turn yellow with age, etc., and are particularly useful in the case of coated papers, by affording means of determining the amount and quality of coating used.

The proportion of ash is found by incinerating a weighed quantity of paper in a platinum crucible. This gives the amount of mineral matter contained in the paper, which, in excess of certain limits for each class of papers, must be considered nothing but an adulterant. An examination of this ash gives the nature of the mineral loading. The proportion of rosin size present is found by a method based on its extraction from the paper by ether, and animal size (glue, gelatin, casein, etc.) by a modification of the well known Kjeldahl determination of nitrogen.

The character, quality and amount of size used are important, as the lasting and waterproof qualities of the paper, as well as its ability to take ink well, are largely dependent on them. Tests for acid are important in papers which are used to wrap metalware of any kind, as acids tend to tarnish anything with which they come in contact. Tests revealing sulphur or chlorine are of value as indicating that the pulp has not been completely freed from the liquors used in its manufacture or in bleaching it; they are, of course, detrimental to the lasting qualities of the paper. Starch is a sizing material sometimes used.

ESTIMATION OF OIL OF PEPPERMINT IN SPIRIT OF PEPPERMINT.*

By CHARLES H. LA WALL, PH. M., and LEROY FORMAN.

The estimation of oil of peppermint in spirit of peppermint has usually been carried out by means of the precipitation method as used for spirit of lemon, using a Babcock milk flask with a graduated neck. The varying results, however, which have been obtained have caused criticism of the method as inaccurate, and upon investigation of the subject we have found that the fault lies not with the principle of the method but with the manner in which it is carried out. The use of a Babcock milk flask, holding as it does only a little more than 25 cc. of liquid, does not permit of sufficient dilution with water in preparations containing a high amount of alcohol and a low amount of oil, for peppermint oil is distinctly more soluble in diluted alcohol menstrua than is lemon oil, to which the method is particularly applicable in its form adopted in the

*From paper read at the Nashville, Tenn., convention of the American Pharmaceutical Association.

United States Department of Agriculture Bulletin No. 107.

Experiments have shown us that where the alcoholic strength is reduced below 25 per cent, the amount of oil dissolved is negligible in amount, but the use of so small a proportion of the spirit in a Babcock milk bottle makes the separated volume of oil so small in amount as to seriously interfere with the sensitiveness of the method to within one or two per cent.

A larger form of flask was designed by us which gives very good results and which consists of a conical flask of 100 cc. capacity terminating in a long narrow tubular neck not over 12.5 mm. in diameter and graduated up to 10 cc. in one-tenths.

The introduction into such a flask of 25 cc. of spirit of peppermint, followed by the addition of 5 cc. of hydrochloric acid and sufficient warm water to fill the flask and bring the oil up into the neck, suffices for the determination within one-tenth of one per cent upon all strengths from 10 per cent down to 1 per cent, all in strong alcohol. The addition of salt which was thought would be of value in hastening the separation of the oil is not permissible, for in the salting out by such a process some of the alcohol is separated with the oil and the results run high to the extent of several per cent in the several experiments tried.

With such a flask, gravitation alone suffices to bring the oil up into the neck of the flask within several hours, occasionally rotating to lessen the tendency of the globules to adhere along the sides of the flask and neck. If the flask were constructed, as could easily be done, so as to permit of whirling in a centrifuge, the estimation could be made accurately and satisfactorily within a very few minutes.

Such flasks are in use by us for the determination of all of the spirits of oils lighter than water, excepting almond, and the additional advantage is gained that after the volume of the separated oil has been accurately observed and noted, the oil itself may be easily and completely removed by means of dry filter paper or blotting paper inserted in rolled strips, without the removal of any of the hydro-alcoholic liquid beneath. The contents of the flask after the removal of the oil may be transferred to a distilling flask, the hydrochloric acid neutralized and the alcoholic distillate from 25 cc. of the original spirit obtained in better condition, as regards freedom from oil, than usually results by following the official method of diluting the original spirit and filtering through magnesium carbonate which always occasions a slight loss by evaporation which cannot take place to the same extent under the procedure given above.

A movement is on foot in Chile to erect a sugar beet factory. Sugar beets have been raised successfully at several points in this republic, yielding 15 per cent and more of sugar.

A RAPID AND ACCURATE GRAVIMETRIC METHOD FOR DETERMINING FAT IN ICE CREAMS, CEREALS AND CHOCOLATE.

In the Journal of Industrial and Engineering Chemistry, 5, 131, E. P. Harding and Guy Parkin described a method for determining milk-fat in evaporated milk and milk powders at the conclusion of which they stated that the method was at that time being tried out on various ice creams, on cheese, cereals, flours and various other products. In the Oct., 1913, issue of the Journal they present a paper giving a continuation of that work. As the amount of the substance used in an analysis, its nature and fat content differ from those of the milk products, the method will be given again somewhat in detail.

A. THE DETERMINATION OF FAT IN ICE CREAM.

The reagents used are acetic acid, 25 per cent by volume; carbon tetrachloride, redistilled; 95 per cent ethyl alcohol, redistilled; and redistilled petroleum ether with boiling point 50° C. to 70° C.

The apparatus used is a 100 cc. Nessler jar or any convenient 100 cc. extraction tube with two rubber stoppers, one unperforated and used while shaking, the other doubly perforated carrying blow-off tubes, similar to the Kerner-Schmidt blow-off tubes but with a double bulb rubber air-pressure pump for forcing the ether layer out of the extraction jar. A 11 cm. filter paper, funnel and stand, wide-mouthed flasks of 50 to 75 cc. capacity for weighing the fat, a small evaporating dish for holding wash petroleum ether, a petroleum ether wash bottle, a condenser, and a drying oven.

The process in detail is as follows: The ice cream is melted by warming to 50° C. and well mixed, without churning, to form a uniform sample. Five grams of this mixture are weighed into the 100 cc. extraction jar, 5 cc. of 25 per cent acetic acid added, and the contents warmed to about 50° C. by cautiously rotating the jar over a low flame or by placing it in a water bath at that temperature. When the protein has dissolved, 12 cc. of carbon tetrachloride are added and the jar vigorously shaken for two minutes. Ten cc. of alcohol are added, the jar again vigorously shaken, then 35 cc. of petroleum ether are added and the vigorous shaking continued one minute. The jar is then allowed to stand from one to two minutes when the separation will be complete. (If an emulsion forms it can be broken up with a few drops of alcohol). The blow-off tube is then inserted and the ether layer, cautiously blown onto the filter which filters through onto the tared flask. (In blowing off the ether layer care must be taken that none of the carbon tetrachloride layer is blown off which may happen if a too close separation of the two layers is attempted. This may be avoided with reasonable care in the manipulation). Five cc. of carbon tetrachloride are then added to the contents of the jar which is thoroughly shaken, then

30 cc. of petroleum ether are added, the jar again thoroughly shaken, one minute allowed for separation and the ether layer blown off with the necessary precautions as above stated. Another addition of 5 cc. of carbon tetrachloride and 30 cc. of petroleum ether is made with thorough shaking after each addition, and the separation of the ether layer after one minute standing is repeated as in the first blow off. Five cc. of petroleum ether are then placed in the small evaporating dish and gently drawn into the jar by sucking on the blow-off tube; after a few seconds this ether which has mixed with the thin ether layer in the jar is blown off through the filter. The filter paper is then well washed with small portions of petroleum ether, about 15 cc. in all, the flask connected with the condenser, the ether distilled off, and the flask heated

for one hour (to constant weight) at 100° C. in the drying oven, then weighed.

During the process while the jar is being prepared for the second and third blow offs, the weighing flask is connected with the condenser and most of the ether distilled off. This shortens the process to about one and one-half hours and permits the use of a 50 to 75 cc. flask for weighing the fat.

CONCLUSION.

The method is recommended for determining fat in ice cream because:

I. It is a short, practical gravimetric method readily adapted to commercial control work, requiring from one to one and one-half hours for a complete determination.

II. It gives a pure fat.

III. It gives a larger per cent of fat when compared with standard methods.

IV. It will give accurate results without a close adherence to the amounts of reagents used.

B. DETERMINATION OF FAT IN CEREALS, COMPOUND CEREALS, FERTILIZERS AND CHOCOLATES.

The method used in the determination of oil in cereals, compound cereals and fertilizers with one ex-

TABLE I.—RESULTS SHOWING THAT A FOURTH BLOW OFF IS NOT NECESSARY.

Sample No.	1st, 2d and 3d Blow offs		4th Blow off	
	Grams weight	Per cent fat	Grams weight	Per cent fat
I.....	0.3909	13.03	0.0003	0.01
II.....	0.3303	11.02	0.0012	0.04
III.....	0.3378	11.29	0.0009	0.03
IV.....	0.3601	12.00	0.0003	0.01
V.....	0.2741	9.14	0.0066	0.02

TABLE II.—RESULTS OBTAINED ON VANILLA ICE CREAMS. 1

The Roese-Gottlieb Method as given in Circular 66 and the Babcock Method as given in Leach were used as comparison methods.

Sample No.	Harding-Parkin			Roese-Gottlieb			Modified Babcock
	Sample weight Grams	Grams fat	Per cent fat	Sample weight Grams	Grams fat	Per cent fat	
389	3.00	0.3375	11.25	3.00	0.3387	11.29	10.00
389	3.00	0.3363	11.21	3.00	0.3312	11.04	10.00
389	3.00	0.3378	11.29				
395	3.00	0.3307	11.02	3.00	0.3303	11.01	10.00
218	3.00	0.3601	12.00	3.00	0.3540	11.80	11.00
218	3.00	0.3612	12.04	3.00	0.3580	11.93	11.00
219	3.00	0.2741	9.14	3.00	0.2755	9.18	8.00
233	3.00	0.2804	9.34	3.00	0.2787	9.29	
231(a)	3.00	0.2897	9.65	3.00	0.2850	9.50	7.00
X	3.00	0.2251	7.50	3.00	0.2250	7.50	6.00
Y	3.00	0.2338	7.79	3.00	0.2261	7.53	
Z	3.00	0.2404	8.01	3.00	0.2350	7.83	
1	3.00	0.2438	8.12	3.00	0.2415	8.05	
11	3.00	0.2493	8.31	3.00	0.2419	8.06	
III	3.00	0.2379	7.99	3.00	0.2394	7.98	

(a) Determination was made on a soured sample.

TABLE III.—RESULTS ILLUSTRATING CHANGE IN BUTTER-FAT CONTENTS OF VARIOUS PARTS OF AN ICE-CREAM PACKER AFTER STANDING.

The samples were two gallon packers which were well filled and in a fresh frozen condition when first sampled. The second sampling was made after the packer had stood twenty-four hours without disturbing at room temperature.

Sample No.	Fresh frozen condition.			After standing 24 hours.		
	Top, Per cent fat	Middle, Per cent fat	Bottom, Per cent fat	Top, Per cent fat	Middle, Per cent fat	Bottom, Per cent fat
I.....	12.17	12.19	12.05	12.38	12.21	12.12
II.....	12.66	12.31	12.63	12.61	12.57	12.11

TABLE III.—RESULTS OBTAINED ON GRAHAM FLOUR, BUCKWHEAT FLOUR, COMPOUND CEREALS AND FERTILIZERS.

The sixteen-hour ether extraction method as given in Food Inspection and Analysis by Leach was used as a comparison method.

Sample No.	Harding-Parkin.			16-hour ether extract.		
	Flour, Grams	Oil, Grams	Oil, Per cent	Flour, Grams	Oil, Grams	Oil, Per cent
I.....	2	0.0518	2.59			
I.....	2	0.0521	2.60			
I.....	2	0.0529	2.64			
I.....	2	0.0535	2.67			
II.....	2	0.0422	2.11	2	0.0410	2.05
III.....	2	0.0311	1.56	2	0.0300	1.50
III.....	2	0.0310	1.55			
IV.....	2	0.0492	2.46	2	0.0482	2.41
IV.....	2	0.0476	2.38	2	0.0475	2.37
IV.....	2	0.0505	2.52			
IV.....	2	0.0493	2.46			
IV.....	2	0.0494	2.47			
IV.....	2	0.0490	2.45			
IV.....	2	0.0477	2.38			
IV.....	2	0.0498	2.49			
IV.....	2	0.0510	2.55			
IV.....	2	0.0497	2.48			
V.....	2	0.0490	2.45	2	0.0478	2.39
V.....	2	0.0492	2.46			
VI.....	2	0.0372	1.86	2	0.0385	1.92
VI.....	2	0.0361	1.80			
VII(a).....	2	0.0630	3.15	2	0.0590	2.95
VIII(a).....	2	0.0504	2.52	2	0.0500	2.50
VIII(a).....	2	0.0516	2.58			
IX(a).....	2	0.0540	2.70	2	0.0533	2.66
X(b).....	2	0.0760	3.80	2	0.0774	3.87
X(b).....	2	0.0744	3.72			
X(b).....	2	0.0740	3.70			
X1(c).....	2	0.2128	10.64	2	0.2127	10.63
X1(c).....	2	0.2371	11.85	2	0.3360	11.80

(a) Determination on buckwheat flour.

(b) Determination on compound cereals.

(c) Determination on fertilizers.

¹See also results obtained on chocolate ice creams.

ception was the same as that applied to ice creams. It was found that acetic acid would not cut the fiber and liberate the oil quantitatively. The same volume of hydrochloric acid with a specific gravity of 1.12 was substituted for the acetic acid with quantitative results.

The method as applied to chocolate was the same as that applied to cereals with the exception that it was necessary to centrifuge two minutes in obtaining the first separation. The following data will show that the Bigelow and Albrech method gives higher results but the extract upon evaporation contained fibrous material which it was impossible to filter off and therefore weighed as oil.

TABLE IV.

The following data were obtained showing a fourth blow off to be unnecessary.

Sample No.	1st, 2d, 3d Blow offs.		4th Blow off.	
	Oil, Grams	Oil, Per cent	Oil, Grams	Oil, Per cent
207	0.0422	2.11	0.0012	0.06
203	0.0630	3.15	0.0008	0.04
211	0.0516	2.58	0.0006	0.03

TABLE V.

The following results were obtained on chocolate. The Bigelow and Albrech Method as given in the Proceedings of A. C. A. C. Bull. No. 137, pp. 102-3, was used as a comparison method.

Sample No.	Harding-Parkin			Bigelow-Albrech		
	Chocolate, Grams	Cocoa Butter, Grams	Cocoa Butter, Per cent	Chocolate, Grams	Cocoa Butter, Grams	Cocoa Butter, Per cent
173	2.00	1.0393	51.96	2.00	1.0720	53.60(a)
173	2.00	1.0341	51.70(b)	2.00	1.0680	53.40(a)

(a) This cocoa butter had a dirty appearance and contained chocolate fiber.

(b) The refractive index of this fat was found to be 1.4575 at 40° C.

CONCLUSION.

I. The method extracts all the oil from cereals and fertilizers and requires but two hours for a complete determination. Other reliable methods require sixteen hours of extraction.

II. It extracts from chocolate all the oil in a pure, fibrous-free condition.

The following table abstracted from a U. S. Consular Report, shows the amount and destination of the rubber shipped from the Amazon River district during October, 1913, as compared with October, 1912:

Exported to—	October, 1913				October, 1912.
	Para.	Manaos.	Iquitos.	Total.	
	Pounds.	Pounds.	Pounds.	Pounds.	Pounds.
United States....	2,028,407	1,448,144	205,969	3,682,519	5,306,945
Europe	1,859,746	1,415,396	38,253	3,313,396	3,725,712
Total	3,888,153	2,863,540	244,222	6,995,915	9,032,657

Prices during the month have been low, and financial conditions continue unpromising.

The Government of the State of Para has practically decided to impose a new surtax on articles exported, the amount of which on rubber will be 100 reis per kilo (1.47 cts. per lb.).

PLUMBAGO SITUATION IN CEYLON.

The surprising increase in the price of plumbago, or graphite, during the last year appears to have led to some misapprehension in the iron and steel trade throughout the world as to the real causes for it. In Ceylon especially the price has risen beyond all expectation, and European importers have been inclined to place the blame on local shippers. The U. S. Consul of Colombo reports that the three reasons assigned locally are the severe floods of 1913, the increased expense of mining as the mines increase in depth, and the shortage of labor.

The following comparative figures, taken from the books of one of the largest exporting firms in the island, show the rise in plumbago prices.

Quality—	January, 1912.	January, 1913.	October, 1913.
	Per ton.	Per ton.	Per ton.
Medium lump	\$ 85.97	\$123.27	\$162.20
Superior flying dust.....	45.42	68.13	113.54
Common dust	25.95	26.76	66.50
Medium ordinary lump.....	97.32	134.63	197.88
Superior chip	94.08	131.38	194.61
Superior ordinary lump.....	154.09	178.42	235.18

¹58 to 60 per cent carbon test.

²56 to 57 carbon test.

Uncured plumbago that ordinarily commands about \$88 per ton now bring \$162 to \$195. Recently as much as \$260 per ton has been paid for uncured plumbago. The character of this lot was above the ordinary, but after curing 13 hundredweight of lump is the best that can be got out of it, and to show a working margin of profit this must bring at least \$373 per ton on the market here, a price that the best lump has not yet reached by over \$113.

In the opinion of Colombo shippers the only solution of the difficulty is for all mine owners to abandon as far as possible the old methods and old machinery and equip their mines with modern machinery. The most necessary machine is a mine pump that will pump out 2,000 to 3,000 gallons per hour with an engine of 25 to 35 horsepower to run it. At present there is one American pump in the island of a type that gives entire satisfaction. It uses 320 ft. of 9-in. piping and pumps 2,000 gals. per hour, with an English-made Horsby-Ackroyd 20-hp. engine. The supply of plumbago near the surface has been practically exhausted throughout the plumbago district and the mines in going deeper to get more material have naturally encountered more water. Buckets and hand pumps and coolie labor have been unable to cope with the inflow.

Plumbago is the most important mineral export from Ceylon, and more than one-half of the total output is taken by the United States. In 1912 the total exports were 654,650 hundredweight, valued at \$2,782,262. The United States took 310,255 hundredweight, valued at \$1,318,587, while Germany took 162,866 hundredweight, valued at \$692,265; the United Kingdom and Belgium took the remainder. Ceylon plumbago is distinguished by its high percentage of carbon and is regarded as the best known for use in the manufacture of crucibles.

METALLURGY.

THE FIXATION OF NITROGEN BY MIXTURES OF BARIUM OXIDE AND CHARCOAL.*

*From the Journal of Applied Chemistry.

By THOMAS EWAN, M. SC., PH. D., and THOMAS NAPIER.

In 1860 Marqueritte and de Sourdeval (Comptes rend., 50, 1100, 1860) announced without further detail that a mixture of baryta and carbon, when calcined in presence of atmospheric air, combines very readily with nitrogen. The reaction was again studied by Mond in 1879 (this J., 1889, 505). He found that the formation of cyanide requires a temperature of at least $1,200^{\circ}$ C. and proceeds most readily at $1,400^{\circ}$ and that 40 per cent of the barium may be cyanized without difficulty. Barium cyanide is not acted on by carbon monoxide, but is destroyed by carbon dioxide at high temperatures. At the temperature of the reaction barium carbonate fuses and must be mixed with sufficient carbon to form an infusible mixture.

Hempel (Ber., 1890, 23, 3388) made a few experiments on the effect of pressure on the reaction, by heating a mixture of barium oxide and charcoal electrically in nitrogen at pressures varying from 1 to 60 atmospheres. The percentage of the barium cyanized increased rapidly with the pressure.

A considerable improvement in the technology of the process was made by J. B. Readman (Eng. Pat. 6621, 1894) by the application of the electric furnace for the production of the high temperature required. The process in this form was worked by the Scottish Cyanide Co. for some years.

The discovery that a large part of the nitrogen fixed is in the form of barium cyanide, BaCn_2 , was first published by Frank and Caro (Eng. Pat. 25, 475, 1898).

The recent experiments of Kühling (Ber., 1907, 40, 310) and Berkhold (Ber., 1908, 41, 28) have shown that the action of nitrogen on a mixture of barium carbonate and charcoal begins at about 950° C., the quantity of nitrogen fixed increasing rapidly with the temperature. The addition of small quantities of barium chloride to the mixture has little or no effect on the fixation of nitrogen, whilst large quantities diminish it. According to N. Caro (Ger. Pat. 212, 706, 1907) alkali or alkaline earth fluorides accelerate the reaction and make it possible to work at 900° to $1,100^{\circ}$ C., and a similar claim is made for potassium carbonate by Snodgrass in a Transvaal patent of 1907.

Our experiments were begun early in 1909 in order to find out whether, with the help of a suitable catalyst, it is possible to fix nitrogen by the barium process without resorting to the very high temperatures hith-

erto employed. We began by studying the behavior of our pure barium carbonate, in very much the same way as Kuling and Berkhold, with whose work we were not, however, acquainted at the time.

A mixture of two parts of pure barium carbonate and one part of well burned wood charcoal, made by grinding the constituents together in a mortar, was placed in an iron boat which was heated in a porcelain tube in a current of dried nitrogen. The supply of nitrogen was regulated so that two liters of gas were collected at the exit end of the porcelain tube in two hours. The regulation and measurement of the temperature of the boat were very troublesome. In the early experiments the porcelain tube was heated in a gas-fired furnace in which different parts of the tube differed in temperature by 50° C. or more; by exploring the tube with a thermocouple before each experiment it was possible to find a region of fairly even temperature in which the boat and thermocouple were placed. The platinum-rhodium couple, enclosed in a quartz tube, was placed inside the porcelain tube and as near the boat as possible; the quartz, however, soon becomes porous under the combined action of the high temperature and of vapors containing barium compounds and the platinum wires are then acted on becoming very brittle. The E. M. F. of the couple changes rapidly and requires frequent calibration. These difficulties were overcome by using a Heraeus electric furnace in which the distribution of temperature along the tube does not change from day to day. The thermocouple was placed in the annular space between the porcelain tube and the tube on which the platinum foil resistance is wound. The boat occupied the central 2 inches of the heated tube, which was 12 ins. long; the greatest difference of temperature in the central 2 ins. was 9° and the couple outside the tube read 5° higher than inside. The melting points of antimony, 624° ; sodium chloride, 798° ; sodium carbonate, 852° , and potassium sulphate, $1,066^{\circ}$, were used in standardizing the pyrometer.

In the experiments the results of which are given in Table 1, the current of nitrogen was passed for two hours from the time at which the required temperature was reached, the boat was then allowed to cool off in an atmosphere of nitrogen. About three minutes were required to raise the temperature from 900° , at which the absorption of nitrogen just begins to the experimental temperature. The whole of the gas collected, consisting essentially of carbon monoxide and nitrogen, was analyzed, and also the contents of the boat. The analysis of the product was made by placing the boat in a corked flask full of water until everything was dissolved, after which the solution was filtered quickly and made up to a known volume. In

suitable portions of the solution the total quantity of soluble barium compounds and the cyanide were estimated by titration with normal hydrochloric acid and silver nitrate respectively. Cyanide was estimated in a third portion of the solution by neutralizing it with nitric acid and boiling for about 20 minutes in order to expel the greater part of the hydrocyanic acid; after cooling and adding a few drops of ammonia, excess of silver nitrate is added and the precipitate of silver cyanamide filtered off and washed thoroughly. It is then dissolved in very dilute, cold nitric acid and the solution titrated with ammonium sulphocyanide and iron alum. The barium carbonate in the insoluble residue is dissolved in hydrochloric acid, preferably after burning off the charcoal, and then precipitated

due to the reaction being stopped by the accumulation of carbon monoxide.

In other respects our results agree closely with those of Kühling and Berkhold. They may be summarized briefly as follows: 1. The absorption of nitrogen begins between 900° and 930° . 2. The amount absorbed under the same conditions increases very rapidly with the temperature, for example, if 4 mols. of nitrogen are passed over 1 mol. of BaCO_3 in two hours about 1 per cent of the barium will combine with it at 930° , about 14 per cent at 960° and about 40 per cent at $1,000^{\circ}$. The greater part of nitrogen fixed is in the form of cyanide, at 960° about $2\frac{1}{2}$ per cent of nitrogen used is fixed, at $1,000^{\circ}$ about 10 per cent (under the conditions of our experiments).

TABLE I.

No.	Av. temp. of boat.	Time, hours.	Grams used.	Gas Collected.		Mols. N_2 used to 1 mol. BaCO_3 .	Percentage of BaCO_3 —		Per cent of N_2 fixed as cyanide.	Per cent of the N_2 absorbed.
				% CO .	c.c. N_2 .		Combined with N_2 .	Converted into BaO .		
3.....	860	2	2.781	14.5	1690	5.6	0	13.0	0	0
38.....	933	2	3.105	23.8	1445	3.8	1.03	34.5	6.0	0.25
35.....	960	2	0.565	6.9	1850	28.9	40.7	46.6	5.6	1.4
34.....	955	2	0.566	8.8	1812	26.6	37.3	50.7	10.4	1.4
28.....	960	2	1.110	19.7	1582	11.9	30.4	59.3	1.2	2.5
30.....	960	2	1.291	20.3	1566	10.1	27.6	59.0	13.4	2.6
29.....	963	2	1.340	20.2	1576	9.8	29.9	54.0	16.1	3.0
26.....	961	2	1.416	22.5	1512	8.9	21.9	63.0	15.1	2.4
27.....	960	2	1.577	23.2	1504	7.9	16.8	62.0	21.2	2.1
4.....	971	2	2.624	40.4	1148	3.6	14.0	68.8	17.2	3.9
8.....	969	2	2.787	38.4	1212	3.6	10.1	65.8	24.1	2.8
23.....	961	2	1.335	58.2	88	0.55	1.7	22.7	75.6	3.0
25.....	1000	2	2.786	39.8	1172	3.5	39.3	44.3	16.3	11.2
39.....	1000	1½	2.308	36.7	1266	4.6	36.3	46.5	14.6	7.2
2.....	1070	2	2.720	39.4	1188	4.4	45.0	38.8	16.2	10.3

TABLE II.

No	Aver. temp. of boat.	Time, hours.	Mols. N_2 used to 1 mol. BaCO_3 .	% CO is gas collected.	% K_2CO_3 in the mixture of $\text{K}_2\text{CO}_3 + \text{BaCO}_3$.	Observed.	% of the Ba combined with N_2		% of the N_2 absorbed.
							Calculated.		
9.....	957	2	5.6	35.2	4.7	20.2	16.0		3.6
14.....	963	2	4.3	39.4	7.4	19.4	12.5		4.5
7.....	964	2	5.0	26.9	10.0	26.9	14.7		5.4
15.....	969	2	4.3	44.7	11.5	18.7	12.5		4.4
10.....	966	2	5.6	38.9	16.7	13.2	16.2		2.4
16.....	960	2	6.9	31.8	40.0	8.4	19.7		1.2

with ammonium carbonate, filtered off, washed and titrated with hydrochloric acid.

The results of a number of experiments made in this way are contained in Table I.

The most interesting results of these experiments is that the percentage of the barium cyanized in the same time and at the same temperature is a function of the quantity of nitrogen passed over it. Kühling and Berkhold used the same quantities of barium carbonate and of nitrogen, in each of their experiments, and therefore failed to observe this connection. In our experiments at 960° the quantity of nitrogen passed over the mixture varied from 0.55 to 28.9 molecules per mol. of barium carbonate used, the corresponding increase in the percentage of the barium combined with nitrogen being from 1.7 to 40.7, the percentage of carbon monoxide in the gas collected after passing over the barium carbonate on the other hand decreased from 85.2 to 6.9. This led us to suspect that the reaction is reversible, the small amount of change when little nitrogen is used being simply

The results of a few experiments in which potassium carbonate was added to the mixture of barium carbonate and charcoal are given in Table II as they were made in exactly the same way as those included Table I.

The figures in the column headed "per cent of the Ba combined with N_2 calculated" are the results which would be obtained with pure barium carbonate using the same excess of nitrogen (interpolated from Table I). The addition of quantities of potassium carbonate up to 11 per cent seems to improve the results, but the improvement is no more than would be produced by a difference of 10° or 20° in the temperature, a quantity which falls within the limits of accuracy of the measurements since these experiments were made with the gas-fired furnace.

The conditions under which the reaction occurs in the experiments just described are really rather complicated, the composition of the gas in contact with the mixture changing continuously during the run, so that it is impossible to draw any very certain conclusion

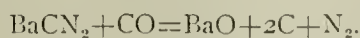
about the nature and course of the reactions which take place. The state of affairs is brought out clearly by a set of four experiments in which equal quantities of the barium carbonate-charcoal mixture were heated for $\frac{1}{2}$, $1\frac{1}{2}$ and 2 hours, respectively, in a current of nitrogen of constant speed. The gas escaping during each 10 to 15 minutes was collected and analyzed, and the solid product was also analyzed at the end of each run. The temperature was the same in all four experiments, about 950° . Carbon monoxide is evolved very rapidly at first. That the maximum quantity is not found at the beginning of the run is due to the arrangement of the apparatus. The boat containing the barium carbonate and charcoal was placed in the center of a porcelain tube which was initially full of pure nitrogen, and about 10 minutes were required for the gases evolved from the boat to reach the exit end of the tube. The hydrogen found is derived partly from the charcoal, which usually contains about 1 per cent of it, and partly from the barium carbonate which, as Finkelstein (Berg. 1906, 39, 1585) has observed, retains small quantities of water very tenaciously.

No cyanide is produced until some 30 per cent of the barium carbonate has been converted into oxide, and the quantity of carbon monoxide in the gas has fallen to about 30 per cent and the percentage of carbon monoxide falls steadily as the formation of cyanide progresses.

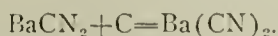
The results above described indicate, as already mentioned, that the absorption of nitrogen by barium oxide and charcoal is reversible. Direct proof of this was obtained by trying the action of pure carbon monoxide on a mixture of barium cyanide and cyanamide which was made by heating dry barium ferrocyanide in vacuo at about $1,000^{\circ}$. The mixture was placed in an iron boat in a porcelain tube which was evacuated and then filled with pure carbon monoxide and heated to 960° for 2 hours. After cooling, the gases were pumped out and analyzed and found to contain 18.2 per cent of CO and 81.8 per cent of N_2 . The compositions of the mixture used and of the product (calculated in gm. molecules per 100 grms. of mixture) were:

	Initial mixture.	Final mixture.	Increase.
Ba(CN).	0.158	0.161	+0.006
BaCN ₂	0.182	0.032	-0.150
BaO	0.087	0.220	+0.133

The principal change which has occurred is, obviously:



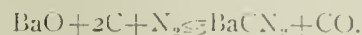
A little cyanamide has also been converted into cyanide,



It does not necessarily follow, however, that carbon monoxide acts on the cyanamide only, because, as will be shown later, cyanide and cyanamide (in presence of carbon) tend towards an equilibrium and relative

quantities depending on the quantity of barium oxide present.

We may assume, therefore, that the fixation of nitrogen is due to one, or both, of the reversible reactions:



If barium oxide, cyanide, cyanamide, and charcoal did not mix, but remained as separate phases, then when equilibrium was attained at any given temperature the ratio of the partial pressures of carbon monoxide and nitrogen in the gaseous phase would be independent of the relative quantities of the solid or liquid substances; and if a mixture of barium oxide and charcoal were heated in an atmosphere of carbon monoxide and nitrogen containing less than the equilibrium quantity of carbon monoxide the reaction would go until the whole of the barium oxide was converted into cyanide or cyanamide. If, on the other hand, the barium compounds do mix the ratio of the partial pressures of carbon monoxide and nitrogen in the gas when equilibrium is attained at any given temperature will depend on the relative quantities of cyanide, cyanamide and oxide in the mixture. The latter appears to be the actual state of affairs and we have attempted to determine the relations between the composition of the solid (or fused) mixture and that of the gaseous phase at three different temperatures ($1,000^{\circ}$, $1,100^{\circ}$, and $1,150^{\circ}$).

The method finally adopted was to heat the barium mixture in a current of gas containing carbon monoxide and nitrogen until the gas escaping from the apparatus had the same composition as that entering it. To make sure that equilibrium was really attained two experiments were made with each mixture of carbon monoxide and nitrogen, one in which the initial material contained no combined nitrogen and a second in which it contained much more combined nitrogen than the final product.

For the experiments with nitrogen-free raw material a mixture of pure barium carbonate, charcoal and reduced iron was heated in a vacuum at the temperature of the subsequent experiment so long as gas was evolved; the product always contained a little undecomposed carbonate.

The nitrogenous raw material was made by heating a mixture of dry barium ferrocyanide and charcoal (sometimes with a little reduced iron) in a current of nitrogen at about $1,000^{\circ}$. Analyses of the products so obtained are given in Tables III and IV. The addition of iron to the mixtures was intended to accelerate the attainment of equilibrium between the cyanide and cyanamide as explained later.

The mixture was placed in a wrought-iron boat (lined with magnesia at the highest temperatures to prevent the fusion of the iron in contact with the charcoal) and heated in a porcelain tube in the electric furnace. The temperature was usually kept constant

within 2". A definite mixture of carbon monoxide and nitrogen (freed from oxygen, carbon dioxide and moisture by passing it first over red-hot copper and then through a concentrated solution of caustic potash and finally strong sulphuric acid) was passed over the boat until the composition of the gas was no longer affected. In several cases the product, after cooling, was reground and retreated in order to make sure that no unattacked substance had been enclosed in the fused or semi-fused mass.

In the first experiment the boat was left to cool off, after the experiment, in the stagnant mixture of carbon monoxide and nitrogen left in the tube. We overlooked the fact that the equilibrium changes as the temperature falls and that carbon-monoxide is ab-

down under the surface of the cold mercury. In this way the material was cooled in one or two seconds and also removed from contact with the carbon monoxide.

In order to estimate the error produced by the absorption of carbon monoxide in cooling, analyses of the gas left in the tube were made in three experiments with results shown in Tables III and IV:

No.	Boat cooled	-% CO in gas—		% Co Ab-
		Before cooling	After cooling	Temp. sorbed
97	In cold end of porcelain tube	4.9	4.9	1100 0
100	In cold end of porcelain tube	46.2	32.5	1100 16.8
101	In quartz tube.....	44.1	37.4	1151 8

The quantity of carbon monoxide absorbed could convert 5 per cent of the barium present into carbonate

TABLE III.

Initial mixture, % composition									% of Barium in product in the form of					% of the Ba combined with N	
No.	Ba(CN) ₂	BaCN ₂	BaO	BaCO ₃	Char	Fe	% CO in gas	Hrs. heated	Temp.	Ba(CN) ₂	BaCN ₂	BaO	BaCO ₃	Charge	Product
95....	17.5	16.3	12.9	6.2	20.5	26.6	4.5	1.5 } 1.25 } 1.75 }	1001	37.8	1.8	53.7	6.7	61.4	39.6
96....				58.4	20.8	20.8	5.5	1.0 } 5.0 }	1602	38.6	2.3	52.4	6.8	0	40.9
91....	15.2	14.1	11.1	5.5	17.5	36.6	5.4	2.5 } 2.5 }	1101	32.5	8.8	45.8	12.9	61.4	41.3
92....				60.0	20.0	20.0	5.25	2.0 } 2.0 }	1100	34.1	9.3	45.8	10.8	0	43.4
87....	17.8	18.2	10.4	7.6	19.8	26.2	18.4	2.0 }	1102	31.3	2.5	50.8	15.5	65.3	33.8
88....	16.1	16.3	9.2	6.8	17.7	33.9	18.3	4.0 }	1100	30.3	2.7	48.8	18.1	65.3	33.0
89....				60.3	19.6	20.1	19.2	1.5 } 3.0 }	1100	28.5	5.4	48.3	17.8	0	33.9
93....	17.3	16.1	12.7	6.2	20.0	27.7	46.4	2.0 } 2.0 }	1100	0.9	2.6	67.5	29.1	61.4	3.5
94....				60.0	20.0	20.0	46.4	1.25 } 1 }	1100	1.3	1.9	65.0	31.9	0	3.2

sorbed on cooling. The results of the experiments made in this way are therefore affected by a small error. It is not very serious because the principal change during cooling is the conversion of barium oxide into carbonate. To avoid this error we first tried to obtain more rapid cooling by pushing the boat quickly into the cold end of the porcelain tube; still more rapid cooling was attained by attaching a water-cooled quartz tube to the end of the porcelain tube, by pushing the boat into this, at the end of the experiment, it could be cooled below the reaction temperature in a few seconds. Finally we arranged the porcelain tube vertically and placed the mixture in a small iron gauze basket which was enclosed in a perforated steel capsule supported by an iron rod which passed through a packed gland at the upper end of the tube. The lower end of the tube was fixed into a wide-necked flask containing mercury. At the end of the experiment the capsule and its contents were pushed

in No. 100 and about 2.4 per cent in No. 101. When the quantity of carbon monoxide in the gas is small the error is negligible.

The total quantity of barium found by analysis in the product agreed very closely with that taken (from 1 to 1.5 grms. BaCO₃) the deficit being usually less than 3 per cent, up to 1,150°, therefore the mixtures of barium compounds are practically non-volatile. Carbon and iron were of course always present in the products in considerable quantities, but they were not estimated.

In Table III the results of the experiments in which equilibrium was attained from opposite directions are collected together.

It is obvious from the figures in the last two columns of the table that a true equilibrium is established, the composition of the product obtained with any given percentage of carbon monoxide being practically the same whether the original mixture contains much

combined nitrogen or none. In Nos. 87-94 the product was allowed to cool slowly and therefore contains rather less nitrogen than corresponds with true equilibrium; this does not affect the above conclusions because each pair of experiments is affected equally and in the same directions.

Table IV contains the remainder of the determinations of the equilibrium. These were not made in duplicate, the experiments included in Table III having shown that the absorption of the nitrogen is completed in a comparatively short time.

In a diagram the percentages of the barium combined with nitrogen after equilibrium is reached are

nitrogen in two hours while a further 80 hours are required to carry the conversion to 57 per cent (No. 110, Table IV.) It is therefore possible that true equilibrium in presence of pure nitrogen will only be attained when the whole of the barium is combined with nitrogen.

We have made many attempts to find a theoretical interpretation of these results but without success. An accurate knowledge of the mutual solubility of the compounds is necessary for a proper understanding of the equilibrium and we have not found time to investigate this. The arrest of the reaction at half conversion appears, however, to be most readily ex-

TABLE IV

Initial mixture, % composition										% of Barium in product in the form of					% of the Ba cooling with N		
No.	Ba(CN) ₂	BaCN ₂	BaO	BaCO ₃	Char	Fe	% CO in gas	Hrs. heated	Temp.	Ba(CN) ₂	BaCN ₂	BaO	BaCO ₃	Charge	Product	Cooling	
109....				34.8	43.5	21.7	3.0	4.5	1000	37.5	5.6	42.2	14.7	0	43.1	Hg.	
108....				40.0	40.0	20.0	10.1	6.2	1000	20.6	2.5	62.1	14.8	0	23.1	Hg.	
105....				42.3	38.5	19.2	18.7	5.25	1000	4.6	0.3	80.2	14.8	0	4.9	quartz	
104....				40.0	40.0	20.0	19.4	1.75 2.25	1000	2.0	0.1	81.2	16.7	0	2.1	quartz	
106....				56.5	21.7	21.8	20.8	1 4.7	1000	0.3	0.1	92.2	7.4	0	0.4	quartz	
107....				40.0	40.0	20.0	20.9	4.1 2	1000	3.5	2.3	80.8	13.4	0	5.8	Hg.	
99....				56.5	21.7	21.8	26.4	4	1000	0.7	0.1	96.6	8.6	0	0.8	porcn	
110....				37.7	42.8	19.5	0.1	82.25	1100	21.2	35.9	20.7	22.2	0	57.1	slow	
97....				55.6	23.1	21.3	4.9	2 2	1100	41.4	4.3	46.9	7.4	0	45.7	porcn	
84....	21.8	22.1	12.6	9.2	24.0	10.3	7.2	2	1101	39.7	4.1	40.0	7.2	65.3	43.8	slow	
98....				56.5	21.7	21.8	28.1	1.6 2.0	1100	32.2	1.1	57.9	8.9	0	33.3	porcn	
85....	21.8	22.1	12.6	9.2	24.0	10.3	38.7	2	1102	6.7	6.1	59.0	28.2	65.3	12.8	slow	
100....				56.5	21.7	21.8	46.4	2 1.8	1100	6.6	1.1	78.5	13.8	0	7.7	porcn	
103....				40.0	40.0	20.0	1.6	1.7 2.75	1150	39.7	9.7	34.5	16.2	0	49.4	quartz	
102....				56.5	21.7	21.8	3.1	1.5 1.0	1151	42.5	1.9	51.2	4.4	0	44.4	quartz	
101....				57.8	21.1	21.1	44.1	1.5 1.5	1151	22.5	1.8	61.5	14.2	0	24.3	quartz	

plotted against the corresponding percentages of carbon monoxide.

With one or two exceptions the experimental points lie very nearly on three straight lines which converge towards a point representing the conversion of one-half of the barium oxide into cyanide and cyanamide in contact with pure nitrogen. It is improbable that these straight lines represent the true form of the curves below 1 per cent of the carbon monoxide. Our experiments show that equilibria in which less than 50 per cent of the barium is combined with nitrogen are attained rapidly and easily, but that, for some reason, the speed of fixation of further quantities of nitrogen is extremely small. When, for example, a mixture of barium carbonate and charcoal is heated in a current of nitrogen at 1,100° over 45 per cent of the barium combines with

plained by the assumption that a compound, BaO. Ba(CN)₂ is formed in which the barium oxide is very much less active than the uncombined substance. This would also explain the fact that up to 1,150° the mixture loses nothing by volatilization, whereas barium cyanide itself, as is mentioned later, is readily volatile at much lower temperatures.

Two experiments may be quoted here in order to give some indication of the rate of absorption of nitrogen by a mixture of barium oxide and charcoal. An intimate mixture of 2 grms. of barium carbonate and 1 gm. of charcoal was first heated at 1,100° in vacuo until no further evolution of carbon monoxide occurred. It was then treated with a steady current of nitrogen at the same temperature and the carbon monoxide produced collected at short intervals and measured. The total quantity of nitrogen fixed was

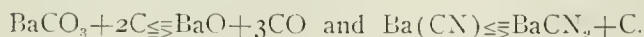
then estimated by analysis of the product. The quantity of carbon monoxide evolved agreed fairly well with the quantity of nitrogen fixed and its rate of evolution therefore afforded a fairly accurate indication of the progress of the reaction. The results are shown in Table V:

TABLE V.

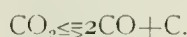
Time of passage of nitrogen min- utes	a		b	
	Per cent of the barium combined with N	Per cent combined per minute	Per cent of the barium combined with N	Per cent combined per minute
10	13.2	1.32	21.7	2.17
20	21.7	0.85	32.0	1.03
30	27.0	0.53	37.5	0.55
40	30.4	0.34	41.5	0.40
60	34.5	0.20	46.0	0.22
80	36.9	0.12	48.2	0.11
100	38.8	0.09	49.5	0.06
120	40.0	0.06	50.2	0.03

In a the quantity of nitrogen supplied per minute was sufficient to combine with 7.5 per cent of the barium; in b it was equivalent to 17.5 per cent per minute. The great increase in velocity produced by an increase in the supply of nitrogen shows very clearly that the reaction itself is a fast one. The diminution of speed which accompanies the conversion of the barium oxide is due partly to the diminution of the available barium oxide and probably partly to the formation of a protective glaze of a readily fusible mixture of barium cyanide and oxide over the surface of the unattacked particles.

Side by side with the main reaction between barium oxide, nitrogen and carbon which has been discussed, two other reactions take place:



The pressure of carbon monoxide in equilibrium with barium carbonate and carbon at any temperature may be calculated from a knowledge of the dissociation pressure of barium carbonate and of the equilibrium.



The initial dissociation pressure of barium carbonate (when less than 10 per cent of it is decomposed) as determined by Finkelstein (Ber. 39, 1585, 1906) is given by the expression

$$\log_{10} p_{\text{CO}_2} = \frac{13860}{T} + \log_{10} T + 8.197,$$

where T is the absolute temperature and p_{CO_2} the pressure of CO_2 in mm. Hg. The pressures of carbon monoxide and dioxide in equilibrium with carbon have been measured very accurately by Rhead and Wheeler (J. Chem. Soc., 1911, 1140). They have expressed their results by an equation which, after some numerical transformation, becomes

$$\log_{10} p_{\text{CO}_2} = \frac{8263}{T} - 0.00067T - 10581,$$

where p_{CO_2} and p_{CO} are the partial pressures of carbon dioxide and carbon monoxide respectively in mm. of mercury and T is the absolute temperature. Combining these two expressions we obtain the pressure of carbon monoxide (in mm. of mercury) which is in equilibrium with a mixture of barium carbonate (very little decomposed) and carbon at the absolute temperature T ,

$$\log_{10} p_{\text{CO}} = - \frac{11062}{T} + 0.5 \log_{10} T + 0.00033T + 9.389.$$

From this expression the following table is calculated:

Temperature (C°)	p_{CO} in mm.
800	9.2
900	77.5
1000	479
1100	2312
1200	9078

From these figures it appears, in accordance with our experience, that the decomposition of barium carbonate must take place to a considerable extent before any barium cyanide can be formed. As Finkelstein has shown the dissociation pressure of barium carbonate falls rapidly as decomposition proceeds owing to dilution or combination with barium oxide and apparently bariumcyanide has a similar effect since when mixed with oxide and cyanide some barium carbonate can remain undecomposed even at $1,180^\circ$ when the pressure of carbon monoxide in contact with it has fallen to a few millimeters.

This equation represents the experimental results very exactly; it does not, however, appear to us to have the theoretical significance which the authors ascribe to it. They write Le Chatelier's general equation in the form

$$\log \frac{c_1^2}{c_2} + \log_e P + \frac{1}{2} \frac{dT}{LT} = \text{const.}$$

Reference to Le Chatelier's original memoir (Ann. des Mines, 1888 (8), 13, 157) shows that the quantity under the sign of integration should be

$$\frac{dT}{LT^2}$$

L being the heat absorbed by the reaction $2\text{CO} = \text{C} + \text{CO}_2$ at constant pressure and not that evolved at constant volume as Rhead and Wheeler have taken it to be. By introducing the value

$L = 38055 + 2.02T - 0.0031T^2$
into the erroneous formula and neglecting the integra-

tion entirely they obtain the formulae

$$\frac{38055 + 2.02T - 0.0031T^2}{T} + \log_e P + \log_e \frac{C_1^2}{C_2}$$

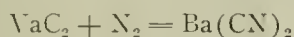
= K which represents their results very well, and has therefore been used in our calculations.

We are unable to give any explanation of the curious fact that the quantity of carbonate remaining undecomposed under otherwise similar circumstances increases with the excess of charcoal present in the mixture (compare Nos. 106 and 99 with 104 and 107, Table IV, also Nos. 102 and 103, Table IV).

It has been assumed that the absorption of nitrogen is preceded by the formation of barium carbide thus:



and



As far as we know this hypothesis was first made in the analogous case of the formation of potassium cyanide from potassium carbonate, carbon and nitrogen by F. R. Hughes (Gram Report of Juries, Exhibition of 1851, I, 95) and again independently by Berthelot in 1868 (Comptes rend., 67, 1141). N. Caro (Chem. Ind., 1895, 14, 289) appears to have been the first to extend the hypothesis to the alkaline earths. We are not aware that any experimental evidence exists showing that barium carbide is really formed under the conditions in which nitrogen is fixed. We therefore heated an intimate mixture of 2 parts of barium carbonate and 1 part of charcoal in an iron boat in a porcelain tube, which was connected to a Topley pump and to a pressure gauge. The temperature of the boat was gradually raised to 1100° the gases evolved being continuously pumped out; after about an hour the quantity of gas collected indicated almost complete decomposition of the carbonate, the pressure was about 3 mm. and it showed little tendency to increase when pumping was discontinued. The temperature was then raised to 1200° and the pumping continued at intervals for 9½ hours, the pressure fell gradually to about 1 mm. of mercury and on lowering the temperature to 1100° it was too small to be read on the gauge. The material left in the boat gave off acetylene when dissolved in water, a quantitative analysis showed that 15.9 per cent of the barium carbonate used had been converted into carbide, 8.3 per cent of it had remained unchanged and the remainder had been converted into oxide. It appears, therefore, that at 1200° the equilibrium pressure of the reaction $\text{BaO} + 3\text{C} = \text{BaC}_2 + \text{CO}$ is about 1 mm. of mercury when only a small quantity of carbide is present, with more carbide it might be smaller but would not be greater.

The approximate equation which Nernst had deduced from his thermodynamix theorem may be used in order to show that this result is at least not im-

probable. For the case under consideration Nernst's equation becomes:

$$\log_{10} p_{\text{CO}} = \frac{Q}{-4.571 T} + 1.75 \log_{10} T + 3.6$$

Where p_{CO} is the equilibrium pressure of carbon monoxide in atmospheres at the absolute temperature T and Q is the heat evolved by the reaction $\text{BaC}_2 + \text{CO} = \text{BaO} + 3\text{C}$. Introducing the values of p_{CO} and T above measured Q is found to be 74,000 cal. from which we obtain the heat of formation of barium carbide from its elements, $\text{Ba (metal)} + \text{C}_2 \text{ (amorph.)} = \text{BaC}_2 + 23,400 \text{ cal.}$ The heat of formation of barium carbide has not been measured, but that of calcium carbide is 19,700 cal. and the following comparison of the heats of formation of some calcium and barium compounds indicates that the difference between them has quite a possible value.

Heat of formation of Ba-heat of formation of Ca compound.

Hydride		-8.7	Cal. per atom metal
Carbide		+3.7	Cal. per atom metal
Nitride		+12.4	
Oxide		-25.5	
Fluoride		-16	
Chloride		+6.1	
Bromide		+10	
Sulphide		-11	
Carbonate		-6	

Using the above value of Q, and calculating p_{CO} in mm. of mercury instead of in atmospheres, Nernst's equation becomes:

$$\log_{10} p_{\text{CO}} = \frac{16250}{T} + 1.75 \log_{10} T + 5.48$$

from which the following table is calculated:

t	T	p_{CO} (mm.)	p_{CO} (atmos.) X 100
950	1223	0.004	0.00056
1000	1273	0.014	0.0018
1100	1373	0.138	0.018
1200	1473	1.0	0.129

The figures in the last column are the same as the maximum percentage of CO which if mixed with nitrogen at atmosphere pressure could exist in presence of barium carbide at the temperatures given in the first column. It is clear, therefore, that barium carbide could not be formed at all in presence of the mixtures of carbon monoxide and nitrogen from which the latter is freely absorbed by barium oxide and carbon, and it cannot be regarded as an intermediate product in the reaction.

It is, however, quite probable that in the analogous reaction with calcium oxide and carbide is a necessary intermediary. For the reaction $\text{CaC}_2 + \text{CO} \rightleftharpoons \text{CaO} + 3\text{C} + 103,200 \text{ cal.}$ Nernst's equation becomes:

$$\log_{10} p_{\text{CO}} \text{ (atmos.)} = \frac{103200}{4.571 T} + 1.75 \log_{10} T + 3.6$$

The substantial accuracy of this equation has been verified by Rothmund (this J., 1902, 761). The equation gives:

$$p_{\text{co}} = 1 \text{ atmosphere at } 2117^{\circ} \text{ C.}$$

$$p_{\text{co}} = \frac{1}{2} \text{ atmosphere at } 2037^{\circ} \text{ C.}$$

The Cyanide Gesellschaft (Eng. Pat. 16298, 1902) states that "nitrogen has no action on a mixture of lime and carbon at 1100° and the reaction $\text{CaO} + 2\text{C} + \text{N}_2 = \text{CaCN}_2 + \text{CO}$ takes place best at a temperature of 2000° , at this temperature only a little of the nitrogen is unabsorbed."

The last statement indicates that at 2000° the partial pressure of the carbon monoxide evolved is about 1 atmo., which agrees very well with the above calculation.

We have finally to consider the relation between barium cyanide and cyanamide and carbon. Our results may be arranged under the headings:

(a) Behavior of pure barium cyanide when heated.

(b) Behavior of barium ferrocyanide when heated.

(c) Composition of products obtained by the action of nitrogen on mixtures of barium carbonate and charcoal.

BEHAVIOR OF PURE BARIUM CYANIDE WHEN HEATED.

Barium cyanide was prepared by A. Joannis (Ann. Chim. phys., 1882 (5) 26, 484), by treating crystallized baryta, $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, with dry hydrocyanic acid until the crystals nearly disappeared, a small excess of the acid was then added to the concentrated solution, which was evaporated in vacuo in the cold until

the hydrate $\text{Ba}(\text{CN})_2 \cdot 2\text{H}_2\text{O}$ was left. This was then heated very gradually in vacuo to 100° . An analysis of the product gave 72.04 per cent Ba and 27.21 per cent CN, which corresponds with 99.29 per cent $\text{Ba}(\text{CN})_2$, 0.18 per cent $\text{Ba}(\text{OH})_2$ and 0.53 per cent water. By following Joannis' directions exactly we always obtained a product containing about 92 per cent of $\text{Ba}(\text{CN})_2$ and 8 per cent of $\text{Ba}(\text{OH})_2$. Even when a cold solution, an analysis of which showed it to contain Ba and CN in the correct proportions, was evaporated in vacuo at a few degrees above zero, the salt deposited contained about this proportion of hydroxide. It is obvious that the saturated solution is hydrolyzed to a considerable extent and free hydrocyanic acid escapes in a vacuum. The impure crystals of the dehydrate can, however, be dried without much further change. This observation led us to a fairly easy method of preparation of the anhydrous salt. Pure, recrystallized barium hydroxide is dried in vacuo, yielding a very fine, dry powder of $\text{Ba}(\text{OH})_2$. This is suspended in dry petroleum ether and an emulsion of anhydrocyanic acid and petroleum ether added to it in about theoretical quantity. In this way the solid hydrate is obtained without evaporation $\text{Ba}(\text{OH})_2 + 2\text{HCN} = \text{Ba}(\text{CN})_2 \cdot 2\text{H}_2\text{O}$. The crystals, when dried in vacuo at a gradually rising temperature, yield a product with only 5 per cent of barium hydroxide and by shaking this with a small excess of dry hydrocyanic acid and petroleum ether and again drying in vacuo a product was obtained containing 97.33 per cent $\text{Ba}(\text{CN})_2$, 0.37 per cent $\text{Ba}(\text{OH})_2$, 1.42 per cent BaCO_3 .

The dry salt fuses at about 600° , it is distinctly vol-

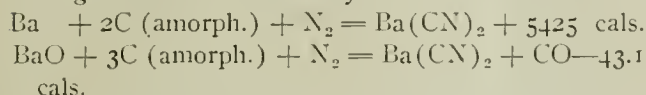
TABLE VI.—COMPOSITION OF PRODUCTS.

No.	Temp.	Time of heating, Hrs. Min.	Mols. per 100 mols $\text{Ba}(\text{CN})_2 + \text{BaCN}_2$			Remarks.
			BaCN_2	BaCO_3	BaO	
58	500	17 50	8.2	11	0	N_2 : nothing volatilised; fritted.
60	550	1	3.2	9.6	0	Vacuum: nothing volatilised; caked but not fused.
62	600	1	11.6	?	?	N_2 : nothing volatilised; semi-fused.
63	620	2	25.4	14.0	7.5	N_2 : nothing volatilised; semi-fused.
64	620	4	29.0	15.4	4.5	N_2 : nothing volatilised; almost completely fused.
70	620	4	63.4	19.3	6.9	N_2 : spongy Fe added; fused.
61	650	1	46.2	1.4	about 8.5	Vacuum: about $\frac{1}{2}$ volatilised; completely fused.
66	700	1	30.7	8.8	10.2	N_2 : nothing volatilised; porous fused mass.
67	700	3 30	30.5	8.4	18.0	N_2 : nothing volatilised; porous fused mass.
59	800	1	41.4	5.2	?	Vacuum: about $\frac{2}{3}$ volatilised; completely fused.
65	800	1 15	29.5	12.5	18.4	N_2 : about $\frac{2}{3}$ volatilised; completely fused.
58	1000	1	53.4	?	?	Vacuum: about $\frac{3}{4}$ volatilised; fused.
69	620	4	13.6	?	4.8	N_2 : Iron boat lined MgO; fritted to hard mass.
71	620	4	12.9	?	2.5	N_2 : Carbon boat; charcoal added.
72	700	2	12.9	?	7.0	N_2 : MgO boat.
73	705	2	25.6	?	3.0	N_2 : Carbon boat; charcoal added.

TABLE VII.

No.	Time of heating (hours)	Temp.	Grams charcoal per gram		Per cent of the barium in the product in the form of				mols. BaCN_2	mols. BaO
			Ba_2FeCy_6	Ba_2FeCy_6	$\text{Ba}(\text{CN})_2$	BaCN_2	BaO	BaCO_3		
1	$2\frac{1}{2}$	580	0	33.7	21.9	43.4	0	1.0	66.5	0
2	$\frac{1}{2}$	850	0	0	36.4	43.7	19.9	0.0	54.7	24.8
3	1	1000	0	0	36.2	41.8	20.0	2.0	53.6	25.6
4	2	1000	0	0	37.4	7.3	50.2	5.0	16.3	112.3
5	1	bright red	0.17	0	31.2	33.9	22.1	12.7	52.1	33.9
6	1	bright red	0.17	0	30.8	30.6	27.9	10.7	50.0	45.4
7	2	850	0.2	0	29.8	16.2	46.2	7.7	35.2	100.4
8	2	850	0.36	0	21.7	12.8	36.2	29.2	37.1	104.9
	1	700								
9	2	850	0.52	0	15.9	2.2	38.2	43.7	12.2	211

atile even at its melting point, for example, a sample lost 42 per cent of its weight when heated for 1 hour at 650° in vacuo, and 65 per cent of its weight when heated for 1¼ hours at 800° in an atmosphere of nitrogen. From Joannis' determinations of the heat of solution of the anhydrous salt and of the heat of neutralization of baryta by hydrocyanic acid, the following heats of reaction may be calculated:



The accompanying table contains the results of a number of experiments in which dry barium cyanide was heated.

Of the above experiments the first 12 were made in iron boats; in every case the product was dark colored, owing to the separation of carbon, but it was noticed that the greater part of the carbon had separated in contact with the iron boat. This led us to try experiment 70 in which an excess of finely divided iron (made by reducing ferric oxide in coal gas) was added to the cyanide. The increased quantity of cyanamide formed is very striking; the only other experiments in which anything approaching to this of cyanamide is formed are those in which a considerable quantity of the material volatilized, if the volatile material is barium cyanide, the relatively large quantity of cyanamide in the residue would be easily understood. In the last four experiments in Table VI, iron was excluded as far as possible. The effect of iron on the change is clearly seen by comparing the four experiments in each of which the barium cyanide was heated for 4 hours at 620°.

No.	Mols. BaCN ₂ in 100 mols. of (BaCN ₂ + Ba(CN) ₂).	Conditions.
69	13.6	Iron boat lined with MgO.
71	12.9	Carbon boat.
64	29.0	Iron boat.
70	63.4	Iron boat; excess spongy iron added.

It is evident that the greater the surface of iron in contact with the barium cyanide, the greater is the quantity of it converted into cyanamide under otherwise similar circumstances. A comparison of Nos. 62, 63 and 64 or of Nos. 60 and 68 shows that the formation of barium cyanamide is very slow, especially at low temperatures, it is therefore probable that the iron merely accelerates this change catalytically.

There is no evidence in these experiments that the reaction $\text{Ba(CN)}_2 = \text{BaCN}_2 + \text{C}$ is reversible. In Nos. 71 and 73, excess of charcoal was mixed with the barium cyanide, but the conversion into cyanamide went as far (or further) than in the parallel experiments 69 and 72 with no charcoal.

PRODUCTS OBTAINED BY HEATING BARIUM FERROCYANIDE.

Barium ferrocyanide is most easily made by mixing hot, concentrated solutions of equivalent quantities of barium chloride and sodium ferrocyanide (if potassium ferrocyanide is used a double potassium ba-

rium ferrocyanide crystallizes out). The salt loses the greater part of its water of crystallization at 160°, but as Drechsel (J. pr. Chem., 1880 (2) 21, 77) observed a little water is retained even at this temperature. By heating 3.328 grms. of the salt, previously dried at 160°, in vacuo at 1050° until decomposition was complete we obtained 26.5 cc. of hydrogen (at 19° and 1 atmo.) which corresponds with 0.6 per cent of water in the dried salt. When the dry salt is heated in a vacuum or in an atmosphere of nitrogen decomposition begins at about 500°, nitrogen is evolved and a mixture of carbon, iron and barium cyanide and cyanamide remains behind. Drechsel had already observed, qualitatively, the formation of barium cyanamide and attributed it to the action of water of barium cyanide, but the quantities produced are much too large to be explained in this way. The compositions of the products which we have obtained by heating barium ferrocyanide, either alone or mixed with charcoal, are given in Table VII.

TABLE VIII.

No.	Temp.	Time of heating (hours)	Mols. BaCN ₂ per 100 mols. BaCN ₂ x Ba(CN) ₂ in the product	Mols. BaO per 100 mols. BaCN ₂ x Ba(CN) ₂ in the product
38	933	2	6.0	3350
35	960	2	5.6	114
34	955	2	10.4	136
28	960	2	1.2	195
30	960	2	4.0	214
29	963	2	5.0	180
26	961	2	2.1	237
27	960	2	5.3	370
4	971	2	8.0	493
8	969	2	7.0	650
33	961	2	0	1340
25	1000	2	5.0	112
39	1000	1½	13.8	128
2	1070	2	11.0	87

TABLE IX.

No.	Temp.	Time of heating (hours)	Mols. BaCN ₂ per 100 mols. BaCN ₂ x Ba(CN) ₂ in the product	Mols. BaO per 100 mols. BaCN ₂ x Ba(CN) ₂ in the product
109	1000	4.5	13.0	98
95	1001	4.5	4.5	136
96	1002	6	5.6	128
108	1000	6.2	10.8	269
105	1000	5.2	6.1	1640
107	1000	4.1	40.0	1390
110	1100	82.2	62.9	36
97	1100	4.0	9.4	103
91	1101	5.2	21.2	111
92	1100	3.1	21.4	106
84	1101	2.0	9.4	111
87	1102	2.0	7.1	150
88	1100	4.0	8.2	118
89	1100	4.7	16.0	160
98	1100	3.6	3.3	171
85	1101	2.0	47.6	461
93	1100	6.0	74.0	1930
94	1100	3.3	60.0	2030
100	1100	3.8	11.3	1020
103	1150	1.4	19.6	70
102	1151	2.5	4.3	115
101	1151	3.0	7.1	253

In experiments 1-3 Table VII, the barium ferrocyanide was heated alone in a vacuum; in No. 4 the product of No. 3 was heated in pure carbon monoxide. In the remaining experiments (5-9) well-roasted

charcoal was mixed with the ferrocyanide and the heating was done in an atmosphere of nitrogen.

(c) Composition of products obtained by the action of nitrogen on mixtures of barium carbonate and charcoal.

Table VIII and IX contain the relative quantities of barium cyanide, cyanamide and oxide contained in the products obtained in the various experiments tabulated in Table I, III and IV. A few results are omitted because the actual quantities of cyanamide were too small to be estimated accurately.

The results collected in Tables VI-IX are best considered together; at first sight they appear to be perfectly chaotic. There is, however, some relation between the percentage of the combined nitrogen which is in the cyanamide form and the quantity of barium oxide in the mixture. This comes out most clearly when the figures in Table VII are plotted graphically. As the mixture is diluted more and more with barium oxide and combined nitrogen passes more and more into the form of cyanide. This seems to be quite independent of the temperature at which the barium ferrocyanide was heated. This regularity does not appear at all in the composition of the synthetic mixtures (Tables VIII and IX). The percentage of the nitrogen in the form of cyanamide in these mixtures appears to have no relation to the quantity of barium oxide present, it is also hardly affected by the temperature. Time may, however, be an important factor; the one experiment in which the mixture was heated for a very long time (82.2 hours in No. 110) gave a result which falls nearly on the curve in the diagram, and the same remarks apply to the experiment in which barium cyanide was heated with finely divided iron (No. 70, Table VI). In the other experiments with barium cyanide the change was obviously incomplete and no regularity could, therefore, be expected.

It may be pointed out that a definite relationship between the quantities of barium cyanide, cyanamide and oxide present in a mixture could only be expected if the three substances were completely miscible and if the reaction $\text{Ba}(\text{CN})_2\text{C} = \text{BaCN}_2 + \text{C}$ were reversible. If the reaction is reversible and either barium cyanide or barium cyanamide forms a solid phase, then there is no necessary connection between the quantities of them present in a mixture because the absolute quantity of a solid phase may vary to any extent without affecting the equilibrium. Our want of knowledge of the mutual solubilities of the nitrogen and oxygen compounds of barium again makes it impossible to give a satisfactory explanation of this reaction. We regret that lack of time makes it necessary for us to leave the question in this unsatisfactory position.

The experiments described were made in the laboratory of the Cassel Cyanide Co., Ltd., and our thanks are due to the directors of the company for permission to publish them.

MODERN OPEN HEARTH STEEL FURNACES.*

By BENJAMIN TALBOT.

During the last quarter of a century perhaps no fact has been more striking in connection with the manufacture of steel than the gradual replacement of Bessemer by open hearth steel. It is well known to all that this extension of the open hearth process is becoming more and more rapid, and as during some considerable time past the author has made a study of the variation in design in the chief forms of furnace used to carry out the process, it has occurred to him that a short paper dealing more especially with the development of the tilting form of open hearth furnace might not be without interest to the members.

It is some 15 years now since the author designed the first tilting furnace erected by him in America. Although tilting furnaces were not unknown at that date, and had indeed been condemned, the furnace erected under his supervision at Pencoyd about the year 1898 embraced several features new at that time. An outline of this Pencoyd furnace, which was rated at 75 tons, is shown in Plate I. It was in this furnace that the first trials of the continuous process were carried out. Although at that time the furnace gave good results, the furnaces which have been erected during recent years under the author's supervision are in many points a very great improvement on his original design.

In studying the design of other furnaces, more especially some of those erected in America, the author has been struck by the seeming want of initiative on the part of modern furnace designers in not studying the possibility of improvements in the design of the tilting type of furnace. He cannot understand the attitude of mind of these engineers unless there is, as he believes, a strong prejudice against this type of furnace. The only alternative that occurs to him to account for their attitude is that they imagine finality has been reached in the design of these furnaces, which would be an absurd position to take up.

This attitude of mind is the more difficult to understand, as several of the large corporations in America have such wide resources and special facilities for experimental work, that they could readily build one or two of these large tilting furnaces in the same shops as their ordinary fixed furnaces, whereby they would be enabled to work under exactly similar conditions of shop practice and materials as their fixed furnace plant is worked under, thereby the question of the respective merits of each type of furnace under varying conditions could be worked out in a practical way, instead of the matter being settled by a committee discussing the question in a purely theoretical way without sufficient practical data before them.

It is to the credit of one of the largest continental

*From a paper read at the Brussels meeting of the Iron and Steel Institute of Great Britain.

steel-making firms that they have adopted this method of practically proving the advantages and disadvantages of each type of furnace, and of varying methods of working.

So far as the author understands, the two main criticisms which are brought against tilting furnaces by those opposed to them are the initial capital out-

by after, say about one-half of the original length of block in the furnace had burnt back, the influence of the water-cooled chill was sufficient to maintain the remaining half in fair working condition. This, however, only mitigated the evil, and the lime dust and oxide and the cutting action of the flame against the block prevented the furnace having a long campaign.

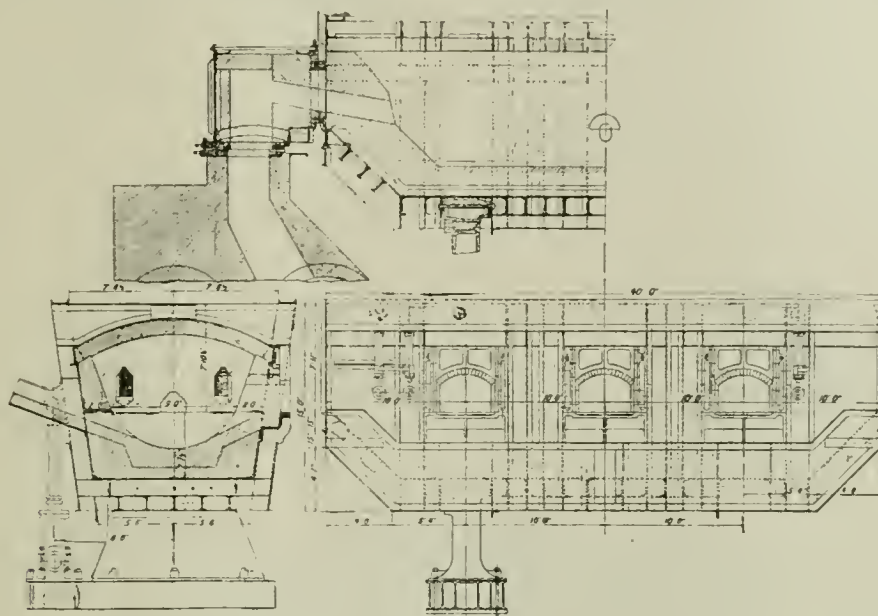


Fig. 1—Rolling Melting Furnace, Pencoyd Iron Works, Pa.

lay and the increased cost of upkeep. In the course of the following remarks the author hopes to combat both these objections, and at the same time to point out some of the salient advantages that accrue from the use of these tilting furnaces, as against the fixed type.

In examining the drawing of the Pencoyd furnace shown in Fig. 1, it will be seen that the furnace is

After trying in various ways to improve the life of the block with more or less success, a radical departure in water-cooling was finally decided upon, and for some time now the furnaces have been built with no block whatever in the tilting section of the furnace itself, the space formerly occupied by the block being now a large central opening in which the incoming air and gas meet and combustion takes place.

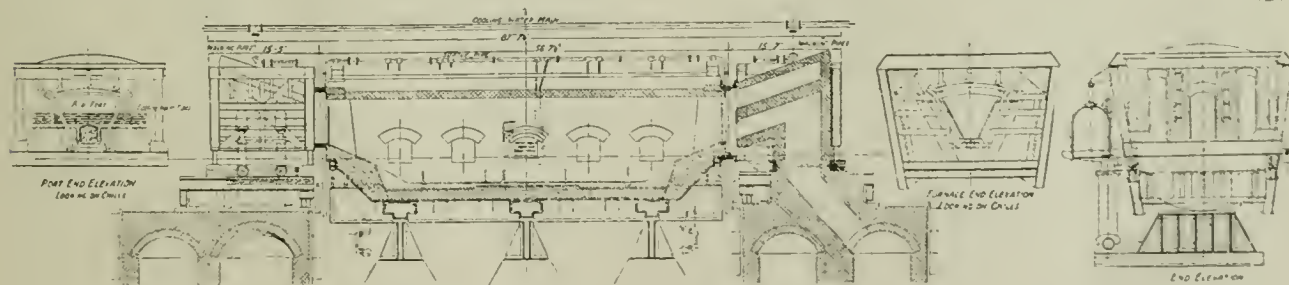


Fig. 2—Arrangement of Talbot Tilting Furnace.

furnished with a block inside the tilting section proper, and in this respect it resembles in every respect the arrangement found in the ordinary fixed furnace. This was found to be the point which gave the greatest trouble in the earlier form of tilting furnaces. Where, as was usual, the furnace was provided with two air and one gas port in the center, it was found that by placing separate water-cooled chills around the opening of each port, both on the tilting section and on the movable port end, equilibrium was established where-

This arrangement is shown in Fig. 2, which also shows the water-cooling arrangements used in connection with it, which cooling arrangements are most essential to the success of the whole. With the port arrangements of the design, shown in Fig. 2, it is quite possible to run the furnace indefinitely as far as the port repairs are concerned. In no other respect has any change of any moment been made in the design of the furnaces as now put down as against those first put down at the Frothingham Co.'s works,

except, of course, that the more recent furnaces put down are of a capacity of 200 to 250 tons, as against the original 75-ton furnace at Pencoyd, and the 100-ton furnace at Frodingham.

To show in what direction others have sought to improve the design of the fixed furnace, the author shows in Fig. 3, the furnace with the Knox cooling devices, which have found wide use in the United States.

These designs show a most expensive form of fixed furnace, although they constitute a distinct advance. If they be carried out, the cost per ton of output with a 60 to 80-ton fixed furnace so designed against a 200-ton tilting furnace, working with the same quality

than those used on the large 200-ton Talbot tilting furnaces, and consequently the cost, apart from the tilting section, cannot be less than that necessary for putting in a large tilting furnace. Again, on analyzing the cost of the various items making up the tilting section, we find that many of them are common to either design; for example, the water-cooled doors, the door framings, cheek pieces, etc., and in modern fixed furnaces the water-cooling devices, are common to both types. It is a fact also that the tilting section, apart from the necessary brick work, is quite a small item in the cost of a complete tilting furnace plant, capable of, say, an output of 1,200 to 1,400 tons of finished steel per week from each tilting furnace.

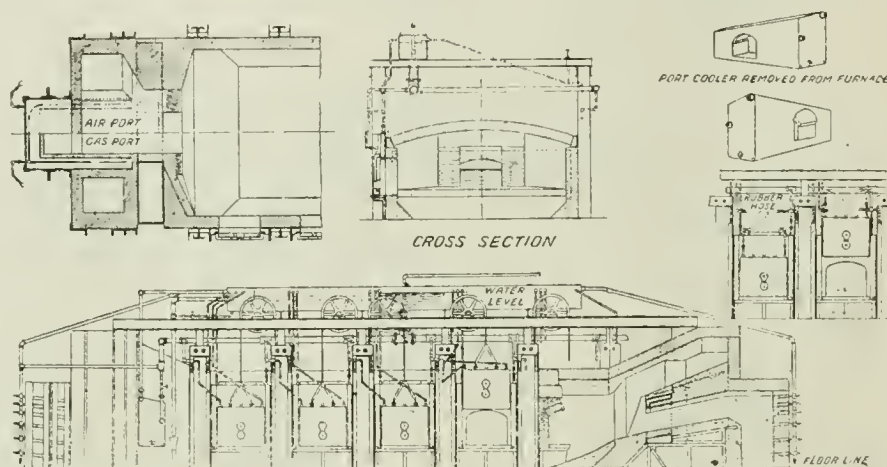


Fig. 3—Knox Patented Water Cooling Device.

of liquid metal and taking out the same weight of cast per heat, will be less in the case of the tilting furnace, since the output from the latter will be larger when working under the same conditions as the fixed furnace.

Again when comparing the tilting furnace with the fixed furnace, especially the large tilting furnaces now commonly used, it must be remembered that the floor space occupied is far less in the case of the tilting furnace per ton of output obtained. This again leads to an economy in the cost of the building which houses the furnaces. Looking at it therefore from every point of view, the author contends, now that such expensive fixed furnaces are being built, which are provided with every appliance that is considered essential in a well-equipped tilting furnace plant, such for instance as charging cranes, overhead casting cranes, ample floor space, arrangements for casting on cars, etc., that the 200-ton tilting furnace will turn out to be a cheaper plant to erect for large tonnage, when regard is had to the quantity of output obtained. In this connection also it is well to remember that it is really only the tilting section in a tilting furnace plant that varies essentially from the fixed furnace plant, as the chambers, flues, etc., are common to and equal in both design. Modern fixed furnaces rated as of 60 to 80 tons' capacity are now being erected in the United States in which the chambers are larger

Looking at tilting furnaces broadly, we find they have found employment in the three following cases:

1. As preliminary refining furnaces.
2. As steel-making furnaces, using either molten metal or cold stock.
3. For the continuous process of steel-making.

In the year 1892 the author designed for the Tennessee Iron & Coal Co. what he believes was the first tilting furnace ever used for the preliminary refining of pig iron.

The pig iron he had to deal with was high silicon and also phosphoric. His problem was to desiliconize the metal in the preliminary tilting furnace and pass on the refined metal for subsequent further treatment in fixed basic open-hearth furnaces. Since that date this use of the tilting furnace as a preliminary refiner has found wide extension. The author quite admits that when very silicious molten pig iron has to be treated, which is not so suitable for direct use in the steel-making furnace, there is much to be said for this use of the tilting furnace as a preliminary refiner. On the other hand, he is of opinion that with a good quality of pig metal, low in silicon and sulphur, much of the pig iron that is passed through these so-called mixers would be very much better retained there and made into steel with one set of men. The question often really resolves itself into a blast-furnace problem rather than a steel-making one. If the blast-furnace manager really cannot make a pig iron sufficient-

ly low in sulphur to treat economically in the steel furnace without an unduly high percentage of silicon, then perhaps the production of a fairly high silicon iron in the blast-furnace, a desiliconization of this iron in a preliminary tilting furnace, and its subsequent treatment in a second steel-melting furnace, is the more economical method of procedure; but the question is a complex one, and the local conditions have to be taken into full consideration.

It is the custom in some works especially in the one the author has in his mind, to treat the metal in the large preliminary refining furnace, and then to pass it along to a basic Bessemer plant, but of this practice the author prefers not to speak.

As to the use of the tilting furnace for finishing off each individual heat, the author has had but little experience of working in this way, as he has found that there is always a tendency for the practical steel melter to keep back some of this charge (steel and slag) to help along the next heat.

As regards the third purpose for which the tilting furnace has been found of use, namely as an apparatus in which the continuous method of steel manufacture is carried out, the author has no hesitation in saying that without the tilting furnace the continuous process would never have been a commercial success, and the millions of tons now being made annually would not have been possible. The ease with which molten pig iron can be poured in, molten steel cast out in any desired quantity, and practically free from all slag, and the facility with which slag can be removed, free from all steel, renders this type of furnace indispensable for carrying out the continuous process. By its use any grade of pig iron (within the ordinary limits of silicon), with or without scrap, can be successfully converted into steel, and any grade of steel from the very softest to the hardest rail quality can be successfully made. From a single furnace of 150 to 200 tons' capacity, with direct molten pig iron only, outputs of 1,200 to 1,500 tons per week of steel ingots are being obtained, and with desiliconized metal from a preliminary refining furnace, 1,800 to 2,000 tons per week, and if blown metal be used instead of pig iron, outputs up to 4,000 tons per week have been obtained from one furnace.

An objection which has been brought forward against the use of large tilting furnaces of 200 ton capacity has been that the objector does not see why 200 tons of steel should be got ready for tapping, and only say 60 to 80 tons taken out. To meet this objection the author has generally asked in reply, does not the fact that you have this tapping temperature, that you have this purity of composition of metal in the bath, and that you have a highly heated basic slag capable of doing work, all tend to quicken the purification of the incoming impure metal as well as to dilute the impurities in it, so that the continuous bath expedites the early part of the charge and thus more than outbalances any disadvantage that may accrue

from retaining a part of the finished bath in reserve? The author has generally found that fair-minded objectors are usually ready to admit that this argument is a sound one, and that when looked at from a debit and credit point of view, the balance is on the credit side.

Another advantage which the use of the continuous bath offers, is that the melter can take off slag at any time that may suit his convenience, and when steels of great variation in composition are being made, such as from a steel with 0.05 per cent carbon to one of 0.70 per cent carbon, this is a very important point.

Again, furnaces can be tapped in better sequence according to the demands of the rolling-mill, and if it is desired for any reason to hold back a furnace and not tap it when ready, sufficient metal can be run in to give additional weight to the bath, and so not lose output whilst still taking off the standard weight of heat in the ladle.

The manipulation of the slag in fixed furnaces when working liquid iron is admittedly not under such good control as when tilting furnaces are used. In fact, we have at one large continental works the peculiar feature of tapping a fixed furnace twice to obtain one heat of finished steel. This method of work must be due to the desire to get rid of the large volume of slag which is formed, unless there is some other advantage of which the author is ignorant, and upon which he would like further information. The furnace is emptied of metal and slag, the hole is stopped, and the metal is returned again to the furnace from the casting ladle. It is true that oxide and lime are added to the furnace before the metal is returned, but they could be added with greater advantage to the surface of the metal if a tilting furnace was employed, and the slag only poured off leaving the metal in the furnace, where it would not be subjected to the cooling action of the atmosphere. The adding of large basic additions chills off the furnace, and in heating up again, accretions form at times on the bottom which grow and cause it to get out of shape. If a tilting furnace were employed with this method of work, no doubt part of the slag would be retained when tapping, and with it necessarily some metal, and the author believes better results would thereby be obtained than by tapping a fixed furnace twice for one product.

The author has given in a series of tables the so-called rated capacities and dimensions of various furnaces, from which it will be seen that there is absolutely no fixed ratio between the rated capacity, the hearth areas, and the cubic areas of the regenerator chambers. The furnaces of 100 tons' capacity and over, are all tilting furnaces using the Talbot process; and it will be seen that in their cases there is a fair agreement between them, but when we come to the fixed furnaces the whole matter is chaos.

As one might from theoretical grounds expect a much higher temperature in the stack from these

large tilting furnaces working the Talbot process, owing to the small cubic capacity of the chambers, the author was interested to ascertain as nearly as possible what this loss really was. A chart of readings taken every five minutes over a period of some seventeen hours by a pyrometer of the temperature at the base of the stack of a furnace of 175 to 200 tons' capacity working continuously, shows an average temperature found, including the high peaks at reversal over the seventeen hours, of 472° C. Omitting the high peaks due to reversal, which can be got over by attention to the valves, the average temperature of the outgoing gases at the stack was 462° C. This compares very favorably with the results given by Mr. Schreiber, who has found for the outgoing gases from a fixed furnace higher temperatures.

The author's desire in bringing before the institute the foregoing remarks, in favor of the extended use of the tilting furnace, has been that it may lead to an interesting discussion on the more modern methods of working the open-hearth process, especially with molten iron, and the most suitable apparatus in which such methods can be best carried out. It may be thought by some that he holds a brief in favor of the continuous process, with which his name is connected, but although he believes the continuous process offers the most economical method of working, he has an open mind on the matter, if a better means of working should present itself. So long, however, as the open-hearth process of converting molten pig iron into steel is found the more economical, he is convinced that the large tilting furnace will ultimately become the apparatus, par excellence, in which much conversion is always carried out when large outputs are required.

NATURAL GAS IN OHIO.

The natural gas industry of the United States prospered in 1911, as shown by the fact that the total quantity produced was practically the same as in 1910, while the value increased from \$70,756,158 to \$74,127,534, a gain in value of 4.76 per cent.

The conditions of production were particularly interesting in Ohio, where three natural gas zones are recognized, the distinctions being important, particularly as the great decline in the northwestern Ohio or "Trenton" field has been compensated to a considerable extent by the rapid development of the Clinton or central Ohio field. The third field is in southeastern Ohio and yields besides gas the light oil of "Pennsylvania grade." The earliest of these fields to be developed was that of northwestern Ohio, where the gas originally found at Findlay furnished the second important field in the industrial development that followed the application of natural gas in manufacturing enterprises.

Gas was discovered at Lancaster in 1887, and further discoveries followed rapidly until the territory

developed into one of the finest gas regions in the country. Moreover, the regularity of the gas sand led to comparatively easy prospecting. The rock structure is fairly simple. In the region of the Bremen field, Fairfield County, the dip is about 57 feet to the mile, with some small rolls having a reverse dip. West of this region the sand thins and disappears before the longitude of the middle of the state is reached, its place being taken by shales. The great reservoirs of gas are usually found near the western margin of the sand, the oil existing at greater depths to the east.

A report recently issued by the United States Geological Survey shows that the year 1911 was one of the best in the history of the natural gas business in Ohio. The central Ohio district, which comprises chiefly the counties of Licking, Knox, Hocking, Fairfield, and Ashland, was actively developed and extended northward into Lorain and Medina counties, many remarkable wells having been discovered, particularly in Ashland County. At the end of the year many of the completed wells were closed in for future use. It is reported that the pressure in the older gas fields of this state is gradually being reduced. In the Homer field, including Knox and Licking counties, the average pressure decreased from 207 pounds in December, 1910, to 180 pounds in December, 1911; in the Sugar Grove field, including Fairfield and Hocking counties, the average pressure decreased from 125 pounds in December, 1910, to 92 pounds in December, 1911. In the new Ashland-Lorain field, however, including Ashland, Medina, Richland, Lorain, and Wayne counties, the average pressure increased from 663 pounds in December, 1910, to 770 pounds in December, 1911, owing to the opening of new territory.

As a consumer of gas in 1911 Ohio takes second place, having consumed 112,123,029,000 cubic feet, valued at \$22,792,270, an average price of 20.33 cents per thousand cubic feet. Ohio consumed more gas for domestic purposes than any other state in 1911, the total domestic consumption being 57,791,210,000 cubic feet, valued at \$15,837,421, an average price of 27.40 cents. The number of domestic consumers supplied increased from 475,505 in 1910 to 577,263 in 1911.

The total quantity of gas produced in this state in 1911 was 49,449,749,000 cubic feet, valued at \$9,367,347 compared with 48,232,406,000 cubic feet, valued at \$8,626,954, in 1910. The difference between the gas produced and that consumed in Ohio shows the quantity piped into the state from West Virginia and Pennsylvania.

The number of gas wells in this state at the close of 1911 remained the same as at the close of 1910, 450 gas wells having been completed and 450 gas wells abandoned during the year. The number of dry holes drilled in 1911 was 191.

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NOTES AND COMMENTS.

President Ira Remsen to Receive the Willard-Gibbs Medal.

The jury selecting the recipient of the Willard-Gibbs Medal, presented by the Chicago Section of the American Chemical Society, has recently designated Ira Remsen of Johns Hopkins University as the recipient of this medal in 1914. President Remsen has recently signified his acceptance of this honor and will address the Chicago Section with their invited guests at the May meeting. His subject has not as yet been announced, but will probably be one of general interest to workers in chemistry.

President Remsen is well known to all American chemists for his research work in various lines of organic chemistry, as a teacher of chemistry and as an author of textbooks in chemistry. He was also the editor of the first chemical journal published in this country.

It seems a fitting tribute to render President Remsen, as he concludes a lengthy service in behalf of the advancement of chemistry in America and retires to the field of the executive where his labors will undoubtedly result in as great benefit to the general field of education as his past labors have to the special field of chemistry.

Dr. Theodore W. Richards Elected President of the American Chemical Society.

The ballots recently counted from the members of the American Chemical Society show the election of Dr. T. W. Richards as president of this society for the coming year.

Prof. Richards is Professor of Chemistry and Chairman of the Chemical Department at Harvard University. He is one of our best known chemists. His most widely known work has been on the atomic weights of various elements. His chemical research has been extensive, however, and has illuminated a number of fields of abstract knowledge in chemistry. Some of his more recent work has been along the lines of: The compressibility of elements in compounds; Accurate Calorimetry and Standardization of Thermometers by Bicomponent System.

Dr. Richards has been honored by many scientific society; one of his most recent honors was to be the recipient of the Willard-Gibbs Medal from the Chicago Section of the American Chemical Society in 1912.

Oil-Hardening Plant in Norway.

Commercial Agent Erwin W. Thompson reports that during the summer of 1913 an oil-hardening plant was opened at Fredrikstad by De Nordiske Fabriker, with head offices at Christiania. The original object was to harden whale oil for the soap industry, but as the result of experiments with edible oils the plant is being enlarged to a capacity of 1,000 barrels a day with the expectation of hardening cottonseed and peanut oils for the margarin makers. If this plan is successful it may double the consumption of cotton-seed oil in the margarin industry. The Norwegian firm will purchase the best grades of cotton-seed and peanut oils, and will also harden on toll.

During the past five years great progress has been made in the hydrogenation of liquid oils, by which process these oils are chemically transferred from the "unsaturated," or liquid, series to the "saturated," or concrete series. Theoretically the process is simple, consisting merely in adding two atoms of hydrogen to the oil molecule; but the means for accomplishing the result have been complicated and expensive, though now growing more simple.

Edible fats with high melting points are higher in price than the others. Hard fats are needed for making hard soaps and artificial lard and butter, and the present natural supply is not adequate. Some apparently successful work is now being done on a comparatively small scale in the United States in hardening cotton oil for artificial lard, and in Europe several plants are operating on various oils for soaps and candles. Many European margarin factories are experimenting on hardening cotton and peanut oils to replace copra oil, which is now very popular and high in price.

Some criticism has been directed at the use of

hardened oils for edible purposes on the ground that nickel is used in the process, but the manufacturers say that although nickel is generally used none of it is left in the oil, and that even if it were it is harmless, as shown by many tests with animals and with human "poison squads."

Wood Alcohol in Germany.

In the report on wood alcohol in Germany published in *Daily Consular and Trade Reports* for September 27, 1913, Consul-General A. M. Thackara, Berlin, states that the prices for August, 1913, f. o. b. Berlin, in usual wholesale quantities, should read as follows:

Methyl alcohol, chemically pure, acetone free, 110 marks per 100 kilos (about 79c per American gallon).

Methyl alcohol, double refined, 88 to 98 marks per 100 kilos (about 63c to 70c per gallon).

Methyl alcohol for technical purposes, 75 to 76 marks per 100 kilos (about \$0.535 to \$0.545 per gallon).

Methyl alcohol for denaturing purposes, 60 to 65 marks per 100 kilos (about 43c to 46c per gallon).

Raw wood alcohol, 58 to 60 marks per 100 kilos (about 41c to 43c per gallon).

Acetone, chemically pure, 150 marks per 100 kilos (about \$1.07 per gallon).

Acetone, double refined, 145 marks per 100 kilos (about \$1.04 per gallon).

Acetone for technical purposes, 127 marks per 100 kilos (about 90c per gallon).

The foregoing prices have been furnished by two of the principal German handlers of methyl alcohol and acetone. Up to December 10, 1913, there had been no material changes in prices.

Lubricating Oils in China.

There has been a notable increase in imports of lubricating oil into China and Hongkong during the last few years, and American oil is largely in control of the situation. The imports of engine oil, as listed in the Chinese customs during the five years ended in 1912, were: 1908, 1,360,472 American gallons, valued at \$259,980; 1909, 1,812,519 gallons, valued at \$327,112; 1910, 2,178,861 gallons, valued at \$414,339; 1911, 2,250,062 gallons, valued at \$424,087; and 1912, 2,391,041 gallons, valued at \$465,518. Of these imports nearly a fourth are imported through Darien for use in northern railway establishments. Hankow takes nearly a fifth for its various industrial and railway establishments, and Shanghai takes about 15 per cent. About a fourth of these imports come direct from the United States, while nearly as much more come through Japan and Hongkong from the United States. Belgium, Germany, Great Britain, and France together furnish about a third of the whole, the importance of their trade being indicated by the order named.

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SCIENTIFIC SEWAGE AND GARBAGE DISPOSAL.

American cities are paying increased attention to the problem of purifying sewage before discharging it into rivers or other convenient bodies of water. The necessity of such purification is generally recognized, but the selection of an economical and efficient method to meet the requirements of a particular city is a difficult matter. Much can be learned from the experiments of the comparatively few American cities that have attempted scientific treatment of sewage, and the methods adopted in certain European cities, especially in England and Germany, are particularly interesting and instructive. For instance, a number of European cities have attempted to meet the expense of purification by selling sludge to farmers and by using liquid sewage on irrigation farms.

The following synopsis of a series of consular reports on the subject of sewage and garbage disposal in Europe aims to show what progress has been made in a number of cities where scientific methods have been adopted. The reports were prepared by the consuls at the request of the commission on sewage disposal of one of the largest American cities. Cities with a population of less than 50,000 have not been included in the synopsis, nor have cities that make no attempt at sewage purification; the latter include nearly all the municipalities of southern and eastern Europe, as well as a few others located near the seashore. Reports from London, Berlin, and Paris were not called for.

Annual reports on the operation of sewage-disposal plants are issued by most of the cities mentioned, and these, together with other details that may be desired, can usually be obtained by addressing the engineering departments of the various cities.

UNITED KINGDOM.

Birmingham Consular District.—In Birmingham the household wastes and street washings flow through the same sewers. More than half the houses of the city are connected with sewers. The sewage is first run into settling tanks and then treated on biological filters. The sludge is treated biologically, rendered inodorous, and afterwards dried on drying beds. The first attempt to eliminate impurities from the sewage was made in 1859, when two precipitation tanks were

built and several acres of land acquired for irrigation. The purification effected was not satisfactory. Several methods of chemical precipitation were subsequently tried, but in 1871 a committee reported adversely on these methods. Since then the tank capacity has been greatly increased, and a much larger area acquired for irrigation. Street sweepings, garbage, and ashes are burned in incinerators.

In Wolverhampton, a city with a population of over 55,000, sinks and water closets are connected with sewers. There are some 10,000 pan closets, which are emptied weekly and the contents, mixed with ashes, sold to farmers. Separate sewers are provided for street washings in about two-thirds of the borough. The sewage is subjected to precipitation with lime, followed by land filtration. The sludge is pressed and sold to farmers in winter and air-dried on land in summer. Septic treatment of sewage was tried, but was considered unsatisfactory.

In Worcester, population about 48,000, sinks and water closets are connected to the same sewers that carry off the street washings. Sewage is filtered through gravel beds and then through sand beds; sludge is used for raising lowland. Street sweepings are sold; house refuse deposited on vacant land.

In Walsall, population 92,000, household wastes and street washings flow into the same sewers. The sewage is treated biologically and the sludge is used for fertilizing. Street sweepings, etc., are tipped on vacant land.

In Dudley, population 52,000, separate sewers are provided for street washings. Sewage is disposed of in two ways: The larger portion is conveyed to a large estate 6 miles from the town and turned onto the land there; the remainder, which can not be disposed of in this way owing to the difficulties of level, is taken by the Stour Valley Drainage Board to their farms and is paid for by the corporation.

In Coventry, population 115,000, sinks and water closets are connected with the city sewers. The newer parts of the city are sewered on the duplicate system. Sewage is treated in tanks and irrigation fields. Percolating filter beds will be constructed soon with a capacity of half the dry-weather flow. The sludge is deposited in beds on the farm and used on the land; it is also given away to farmers. Sweepings, garbage,

etc., are burned. At one time Coventry sewage was purified by chemical precipitation.

Bradford Consular District.—In the city of Bradford, population 288,000, household wastes and street washings are run into the same sewers. The sewage is purified by chemical precipitation and filtration. The sludge is filter-pressed for the extraction of wool grease, the yearly value of grease recovered being about \$250,000; part of the press cake is sold as manure at 74 cents a long ton, and part is used as fuel. The first method of sewage purification tried in Bradford was filtration through peat. Later, lime precipitation followed by filtration through coke was tried, but this method also failed. The street sweepings are tipped onto vacant land, and house garbage and ashes are part tipped and part burned.

In Halifax, population over 100,000, household wastes and street washings flow into the same sewer. The sewage is treated in precipitation tanks and bacterial filters (double contact beds and percolating filters). The sludge is pressed and carted away by farmers. Street sweepings, garbage, and ashes are tipped onto vacant land.

Leeds Consular District.—The city of Leeds has a population of 445,000 and maintains five sewage works. Household wastes and street washings flow into the same sewers. The sewage is subjected to bacteriological treatment after chemical precipitation and the sludge is pressed into cakes and disposed of as fertilizer. Sixty per cent of the house garbage and ashes collected in the city is disposed of in destructors; the remaining 40 per cent is deposited on land as manure or is used to fill quarries. The street sweepings are sold at 18 cents a ton to farmers and market gardeners. For 10 years the city has experimented with practically all the known methods of treating sewage.

In Wakefield, a town of 51,000 inhabitants, located 9 miles from Leeds, the household wastes and street washings are run into the same sewers, although there are a number of special storm sewers to take away surface waters from the streets. The sewage is subjected to chemical precipitation, percolation through bacteria beds, and settlement in humus tanks. The sludge is trenched into land formerly used for filtration purposes. At one time land filtration after chemical precipitation was tried, but the land proved unsuitable.

Previous reports on sewage disposal in Leeds and Wakefield were published in Daily Consular and Trade Reports for October 21, 1910. A detailed description of the methods employed in Wakefield, furnished by the borough engineer, may be had from the Bureau of Foreign and Domestic Commerce, Washington, D. C.

Sewage Farming at Liverpool.—Nine-tenths of the sewage of Liverpool is discharged into the Mersey without treatment of any kind. The remaining one-tenth comprises the sewage of districts known as West Derby and Walton and is treated on the West Derby and Walton sewage farms, the system adopted

being broad irrigation without chemical treatment, but assisted by bacterial and storm-water beds. The West Derby farm has an area of 207 acres and receives the sewage of about 56,000 inhabitants. The Walton farm has an area of 183 acres and receives the sewage of about 61,800 inhabitants. The crops on both farms consist chiefly of rye grass, cabbages, potatoes, mangel-wurzels, and beets.

Manchester Consular District.—In Salford, a town of 231,000, lying opposite Manchester, one system of sewers is used for both household wastes and street washings. The sewage is subjected to chemical precipitation, in which lime and salts of iron are used, and the tank effluent is then passed through roughing filters and finally bacterial filters. The sludge is sent to sea in a 600-ton sludge steamer. Street sweepings are sold as manure, and the house garbage, ashes, etc., are burnt in destructors. Many methods of sewage purification, probably 20 to 30, have been tried in the last 25 to 30 years.

In Oldham, a town of more than 147,000 population, all household wastes and street washings are carried off in the same sewers. The sewage is treated by precipitation, settlement, and contact and sprinkling beds. The sludge is given to farmers. Street sweepings are used as manure, and garbage and ashes are burned in destructors.

Accrington, with a population of 50,000, has the single-sewer system. The sewage is purified in septic tanks and by continuous filtration in percolating bacteria beds. The sludge is sent to the farming districts by canal. Street sweepings are sold as manure and the garbage and ashes are destroyed in destructors.

The single-sewer system is also used in Stockport, population over 100,000. The sewage is subjected to chemical precipitation, land filtration, and oxidation on bacteria beds. The sludge is pressed and disposed of to farmers. Street sweepings and ashes are at present tipped, but a destructor is in course of construction.

Leigh and Atherton, two towns with a combined population of over 66,000, have a single-sewer system in common. The sewage is treated by means of chemical precipitation tanks, land, and filters. The sludge is pressed and sold to farmers. Sweepings, garbage, and ashes are burned in destructors or buried in tips.

In Rochdale, population over 91,000, household wastes and street washings are carried off in the same sewers. The sewage is subjected to sedimentative and bacterial treatment and the sludge is disposed of to local farmers. Street sweepings are sold to farmers and garbage and ashes are burned.

Sewage-disposal System of Sheffield.—Until 1886 the sewage of Sheffield flowed in an untreated condition into the rivers and watercourses. In that year a main sewerage scheme was completed at a cost of \$750,000, and sewage-disposal works were constructed at a further cost of \$220,000, the process adopted being

that of lime precipitation. The works were designed to treat a flow of 10,000,000 gallons of sewage per day, but for several years a flow of 17,000,000 gallons has been dealt with, and since 1886 the population has increased from 304,720 to 470,000, and the introduction of the water-carriage system, the extension of the drainage area, and the increased requirements have necessitated improved methods of treatment in addition to increased capacity. It was finally decided after exhaustive experiments to adopt a scheme consisting of continuous-flow settling tanks and contact beds. The local government has approved of the scheme, which is now partly in operation, and the remainder is approaching completion.

The estimated cost of the extensions was \$1,350,000, but it appears probable that the work will be completed for \$35,000 less than that amount. In addition to this the city has bought lands for the present works and future extensions at a cost of \$430,000.

The principal features of the scheme include a new main valve chamber, into which a 5-foot barrel sewer discharges and also a 7-foot duplicate sewer. A storm-water overflow arranged to discharge the excess flow above 64,500,000 gallons per day to a storm-water conduit is fixed in the chamber.

A large penstock, with opening 5 by 12 feet, admits the sewage to a conduit 12 feet wide, which conveys it to the catch pits. Two pairs of catch pits, 42 feet long, 29 feet wide, and 13 feet deep, have been constructed; they are fitted with new screens, which extend the whole length of the pits and which are cleaned by hand rakes. The catch pits are in the form of a double hopper and retain the heavier grit, garbage, and larger objects. Each pair is fitted with endless-chain bucket elevators for cleansing purposes. Two additional catch pits have been added, approximately twice the size of the older ones, and fitted with mechanical screens and an electrically driven traveling bucket dredger. The sewage passes from the catch pits through branch and main conduits 12 feet, 16 feet, and 20 feet wide, built in brick and covered with girders and concrete to the settling tanks. The complete scheme includes 17 continuous flow settling tanks, each holding approximately 1,000,000 gallons, which are now in operation.

Sixty contact beds, each half an acre in area, and 16 storm beds of similar design but twice the size are in course of construction. The works will provide for the treatment of a maximum quantity of 64,500,000 gallons of sewage a day, and will be one of the largest of its kind.

Sheffield has two extensive garbage destructors, the refuse destroyed in 1912 and 1913 amounting to 42,898 and 33,805 tons, respectively, at a cost of \$28,760 and \$21,450. For dumping 35,663 tons of garbage requiring railway transportation there was expended, in addition to these amounts, \$20,435.

A plant for converting fish refuse into fertilizer recovered 82½ tons during 1913; it was sold at a profit

to the municipality of \$600. There is also a can-bundling plant that handles 300 to 400 tons of used cans a year.

Methods Employed in Belfast, Ireland.—The single-sewer system is in use in Belfast. At one time all sewers emptied directly into the River Lagan, but sedimentation tanks are now used and the purified effluent is stored in ponds until high tide, when the discharge commences. The sludge is pumped into a ferro-concrete loading tank, whence it is discharged into a steamer and carried to sea. Experiments have been made with various systems of sewage disposal, but the city authorities are of the opinion that the method now used is the most economical for a city situated on the seashore. A refuse destructor having 12 cells, each with a capacity of 10 tons per 24 hours, has been constructed. An incinerator furnace has been added, and in this are consumed all infected articles, typhoid excreta, diseased carcasses, fish offal, and other objectionable material. Unobjectionable matter is either used to fill up hollow ground or sold for manure.

Glasgow Consular District.—The single-sewer system is used in Glasgow, Scotland, and the sewage is purified by chemical precipitation; a portion is filtered. A portion of the sludge is filter-pressed; the bulk of it is sent to sea. Part of the street sweepings, garbage, and ashes is destroyed in destructors and part is sold. Reports on the garbage disposal system of Glasgow were published in Daily Consular and Trade Reports for October 21, 1910, and March 12, 1913. A copy of the annual report of the manager of the sewage purification works of Glasgow will be loaned by the Bureau of Foreign and Domestic Commerce.

In Greenock, a town of over 74,000, the household sewage and the street washings are carried off in the same sewer; the sewage is emptied into the river without previous treatment. Street sweepings, garbage, and ashes are sold as manure, tipped onto vacant land, or sent to the destructor, depending on the character of the material.

GERMANY.

Barmen Consular District.—Barmen, a city of 172,000, depends chiefly on the Trennung (divided) system of sewerage, in which the sewer has two parts, the upper and larger for street washings and the lower for household wastes. The street washings are emptied directly into the river. The sewage is mechanically cleared. An experimental plant for further purification has recently been put into operation. Street sweepings are dumped. Garbage and ashes are burned in the municipal garbage-burning plant. The present garbage-burning plant was constructed in 1907 and has given satisfaction in every respect. Not only is the city's garbage disposed of in a sanitary manner, but incidentally a fine quality of sand is produced, and the heat produced by the burning garbage is converted into electricity. The slag is reduced by crushing to various grades of sand that have been used with splendid re-

sults for building purposes and for the manufacture of bricks. The hot gases from the burning garbage are conducted to a boiler, and the steam raised is used to run a steam turbine that is connected with a dynamo. The current developed is sold to the municipal electric works at 0.833 cent per kilowatt hour and is in turn sold to the public at 2.718 cents per kilowatt hour. The plant produces annually 11,000 tons of slag or clinkers from 22,000 tons of garbage, and the electric current produced amounts to 1,700,000 kilowatt hours a year.

Elberfeld, population over 172,000, has the double-sewer system in some parts of the city and the single system in others. The sewage is treated in mechanical settling basins, and the sludge is used for filling in land. Street sweepings, garbage, and ashes are also used for filling in.

In Dusseldorf, population 400,000, household wastes and street washings are carried off in the same sewers. The sewage is purified in a *Fein-Rechenanlage* (fine raking plant), and the sludge sold to farmers. Street sweepings, garbage, and ashes are carted away at present, but a plant for burning such refuse is contemplated, and it is planned to use the waste of this plant in making artificial stone, fertilizer, etc.

The single-sewer system is used in Duisburg, a town of over 244,000. The sewage is subjected to mechanical clearing in basins, and the sludge is dried and used as a fertilizer. Street sweepings, garbage, and ashes are used for filling in land.

Mulheim on the Ruhr, with a population of 120,000, uses one sewer for both street washings and household wastes. The sewage is purified by means of settling basins, filtration through slag, and the "dripping" system. The sludge is used as a fertilizer. Street sweepings, garbage, and ashes are used for filling in land.

In Dortmund, population 233,000, household wastes and street washings are carried off in the same sewers. The sewage is purified on sewage farms (*Rieselfelder*). The sludge is used as fertilizer. Street sweepings, garbage, and ashes are used for filling in land.

In Hagan, population 93,000, household wastes and street washings are carried off in the same sewers for the most part, although in some sections separate sewers are provided for street water. The sewage is treated in settling basins and Emscher wells. The sludge is used for filling in land around the settling plant. Street sweepings, garbage, and ashes are carted to municipal dumps.

The single-sewer system is used in Munster, a town with a population of 93,000. The sewage is purified on sewage farms and the sludge is used as a fertilizer.

Breslau Consular District.—In Breslau, population over 511,000, the household sewage and street washings flow into the same sewers, which discharge into sewage fields owned by the city and leased to private persons. A part of the street sweepings, garbage, and ashes is used for agricultural purposes and the rest for filling up low-lying municipal property.

In Liegnitz, population over 66,000, household and

street sewage flows into the same pipes and is filtered in sewage fields. The sludge is sold to farmers. Garbage and ashes are used for filling.

Household sewage and street washings flow into the same sewers in Gleiwitz, a town of 67,000. The sewage is filtered in sewage fields and the sludge sold to farmers. Street sweepings, garbage, and ashes are used for filling.

Sewage Disposal in Dresden.—All kitchen sinks in Dresden and about two-fifths of the water closets are connected with sewers, and the system is still being extended. The street waters flow into the same sewers as the household wastes. Before being emptied into the river the sewage is freed from solid matter by means of the Riensch-Wurl separationsscheiben system. The sludge is sold to farmers. Attempts are being made to dry such sludge.

The Brunswick Drainage Field.—The household wastes and street washings of Brunswick are carried off in the same sewers, and the sewage is treated on the sewage farm (*Rieselfeld*), which is located about 4 miles from the city. The farm comprises 1,150 acres, of which 579 acres are laid out in beds for raising vegetables and 308 are used for raising grass. The results are said to be superior to those obtained by any other German city, especially Berlin, and the success is attributed to the fact that the water is drained off by underground pipes. Experience at Berlin has shown that underground drainage is absolutely necessary because otherwise the soil becomes matted and foul. The vegetables grown on the Brunswick farm are remarkable for their size, the cabbage heads especially, but the quality is inferior. It is said that when cooked the vegetables reveal the excremental nature of the fertilizer in odor and taste. In consequence they are consumed only by the poorer classes of the population. The farm cost \$644,504.

Disposal of Sewage in Erfurt.—Household and street sewage is carried off in the same sewers in Erfurt, a manufacturing city with a population of 127,000. The sewage is settled mechanically in Emscher wells. The sludge is dried in fields and sold as fertilizer to nurseries, horticultural establishments, and farmers. No other scientific method of disposing of the sewage has ever been tried. The street sweepings and garbage that can not be used as fertilizer are incinerated and the product sold to farmers. The bulk of the ashes collected is used for filling in land.

Hamburg Consular District.—Hamburg, with a population of over 1,000,000, is located on the Elbe River at a point where the tidal ebb and flow amounts to 6.56 feet, and where conditions are such that the current of the river itself is disregarded as an influence in the matter of sewage disposal. Household wastes and street washings flow into the same sewers. The contents of the main sewer, before being discharged into the Elbe, pass through collecting basins in which swinging dredges continually remove solid and floating material, which is then transferred in barges to a low-

lying island in the river, the level of which is being slowly raised. The waste water then flows into the river through three final discharging pipes. Owing to the tides there is a steady circulation of fresh water and a continual churning of the refuse, which facilitates its destruction. No general attempt is made to sterilize sewage at Hamburg. Garbage and ashes are collected in carts and incinerated. Previous articles on sewage and garbage disposal in Hamburg have been published in Daily Consular Reports for October 21, 1910, February 13, 1912, and March 12, 1913.

Harburg, with a population of 67,000, is located on the south branch of the Elbe, opposite Hamburg. Separate sewage systems are maintained for household wastes and street washings, and practically all houses are connected with the sewer system. All waste water is led into a clearing plant, where by means of dredging rakes and cesspools it is mechanically clarified. No other process has ever been employed.

In Rostock, population 70,000, the household and street wastes flow into the same mains, and the sewage is purified in Emscher wells or cesspools. Garbage and city wastes of all kinds are collected and used for filling in land.

Kehl Consular District.—Kehl, a town of 8,800, located on the Rhine nearly opposite Strassburg, has a sewer system to carry off street waters, but household wastes are held in cesspools, which are emptied from time to time and the contents distributed on fields. The sewer wastes are run into settling basins and the sludge is used as a fertilizer. Most of the horse manure on the streets is gathered by children and used in gardens. Other street refuse and ashes are used for filling in lands. House garbage is used for feeding domestic animals.

In Strassburg, a town of 178,000 inhabitants, the household wastes of about three-fourths of the city and all the street washings are carried off in the same mains. A portion of the sewage water is strained and run onto irrigation farms and into fish-culture ponds. Otherwise no attempt has been made to purify the sewage, although experiments are now being made with a view to treating the sewage in a more scientific manner. Street sweepings, garbage, and ashes are sorted and a part sold to farmers, rag pickers, and others, and the remainder used for filling in land.

In Freiburg, population 80,000, practically all houses are connected with sewers and for the most part street washings are carried off in the same sewers. The sewage is first run into settling basins and then onto irrigation fields. The sludge is used for fertilizing purposes. The irrigation fields are divided into sections of about 3 acres each by dams and banks. Half of the field is meadows, one-fourth is devoted to winter grain, and one-fourth to summer grain and vegetables. The crops yield \$34 to \$38 an acre, which means a profit, not including interest, of about \$4.80 an acre. It is calculated that the irrigation plant yields a revenue of two-thirds of 1 per cent on the cost of

the plant. Owing to the favorable character of the soil, 1 acre suffices for 159 inhabitants, whereas in most places using the same system 1 acre is required for every 100 inhabitants. The sewage flowing onto the drainage fields totals about 60,000 cubic yards a day, or about 120 cubic yards a day per acre. About 30 or 40 years ago an attempt was made to dispose of the sludge in the sewage by manufacturing it into poudrette, a dry powdered fertilizer. That portion of the street sweepings, garbage, and ashes that can not be used for fertilizing purposes is used for filling in land.

In Mulhausen, a town of 100,000 inhabitants, the household wastes and street sweepings are carried off in the same sewers, except when the rain is excessive, when the overflow goes into the rivers. The swage is pumped into a canal, or main sewer, about 9 miles long and partly open, where it is mixed with river water. It is then distributed on about 2,320 acres of meadow land. The flow of sewage is about 100 gallons a second and the pumping station has a capacity of 158 gallons a second. The sludge is not separated. The street sweepings, garbage, and ashes are used for fertilizing purposes and for filling in land.

In Metz, population 68,000, the kitchen sinks and about four-fifths of the water closets are connected with sewers, and the street washings are carried off in the same mains. In the past the sewage has not been treated in any way, but the sewers are now being rebuilt and it is intended to adopt some method of purification, probably fresh water and settling tanks. Street sweepings, garbage, and ashes are used for fertilizing purposes and for filling in land.

Stettin Consular District.—The liquid house sewage and the street washings of Stettin, population 240,000, flow into the same sewers and are discharged into the river without further treatment. The solid house sewage is retained in cesspools and carted away. In the near future a new system is to be inaugurated. A mechanical sewage cleaner is being built, fitted with the so-called Rien'sche Scheibe (Riehn's disk), which will remove from the sewage all the coarser matter before it is discharged into the river. The sieve has a mesh of 1.5 mm. (0.05905 inch). After the new system is put in operation the cesspools will be removed. Street sweepings, garbage, and ashes are used for filling in land.

In Danzig, population 175,000, practically all of the houses are connected with sewers, and the sewage is conducted into pools and then onto irrigation fields near the city. The street washings are for the most part discharged directly into the rivers within the city, but a small portion flows into the sewers. Street sweepings, garbage, and ashes are carried to waste fields outside the city.

In Elbing, a town with a population of 65,000, the kitchen sinks and water closets are connected with sewers, and a separate system is provided for street washings. The sewage is treated in filter beds, the sys-

tem being known as Kohlebreiverfahren. The sludge is gasified in generators or sold for fertilizing purposes. Street sweepings, garbage, and ashes are used for filling in land.

In Königsberg, population 260,000, household wastes and street washings are run into the same sewers in the central city, but in other parts of the city separate sewers are provided. Only a part of the street washings flows directly into the river. The sewage is pumped into a ditch (Vorflutkanal), where it passes through two sand filters. The ditch consists of a built-up masonry section 5.1 miles in length and an open ditch section 14.6 miles in length. It empties into the Frische Haff. Alongside the ditch are 12 sludge basins through which the sewage can be led. Four thousand one hundred acres of land are irrigated by the water from the sewage as needed, the remainder passing through two sludge basins before entering the Frische Haff. The sludge is dried and sold to farmers. The efficiency of the filtering is constantly tested. No other method of sewage disposal has been tried. Street sweepings, garbage, and ashes are used for filling in land.

FRANCE.

Method of Purification Employed in Rheims.—In the city of Rheims, with a population of 115,000, the kitchen sinks in the modern buildings are connected with the sewers, and in about 200 of the 13,221 buildings of the city the water closets are also connected. Rain water is carried off in the same sewers. Since 1885 the city has clarified the sewage by irrigation on agricultural land. This purification, which is considered very satisfactory, is effected on fields of a chalky nature comprising some 1,400 acres. The work is carried out by a private company. Previous to 1885 chemical purification was attempted, but proved a failure. The street sweeping, garbage, and ashes are carried away by private contractors, to whom the city pays annually about \$15,000. After sorting, this refuse is sold for fertilizing purposes. The authorities are considering the advisability of changing this method of utilizing the city sweepings.

Brickmaking from City Refuse in the Commune of Villeurbanne.—In the commune of Villeurbanne, adjacent to the city of Lyon, the city refuse is burned and bricks are made from the residue. This has been a private enterprise but the municipality has arranged for the purchase of the crematory. The crematory is a model plant, and annexed to it is a brick pressing plant. The furnace serves not only to burn the refuse, but also to operate, by steam, the various machines in the factory.

The residue from the furnace is first carried through a series of heavy rollers, after which it is delivered in is mechanically mixed with a heavy lime in the form of a fine powder to a mixing trough. Here it portion of 80 per cent of residue to 20 per cent of lime. This mixture is emptied into another longer trough by a system of buckets operated on a chain,

where the proper amount of water is added, and the material is then fed to the brick-pressing machine, which is of English manufacture and capable of turning out 20,000 bricks per day. After 28 or 30 days the drying is completed, but the bricks are as a rule not used for 60 days from the time they leave the press. The only kinds of refuse not used in this manufacture are empty cans, metal barrel hoops, and other similar waste that may easily be sold as scrap metal.

The bricks sell at the factory in ordinary wholesale quantities at \$5.79 per thousand. If ordered in very large quantities, this price is sometimes reduced to \$5.40, or even \$5.02. The bricks are of good quality, strong and durable, and light gray in color. They are said to be especially appreciated by the masons on account of their smooth surface and even edges. It must be understood that the above prices are those of a private concern, which would naturally be interested in making the figures as high as possible. Were the work completed under municipal supervision, the cost of manufacture would be less, and the expense of disposing of the city waste could probably be fairly met by the profits derived from the incineration of the refuse and the building material made therefrom.

AUSTRIA.

Sewage Disposal in Prague.—The sewage from the city of Prague, population 575,000, is conducted through four large sewers to a cleaning plant at Bubenc, one of the suburbs. The sewage is first passed through a system of screens, which catch the coarser materials. The balance of the material then passes along, and is distributed in 10 oblong basins 285 feet long, 18 feet wide, and 9 feet deep, where the solid substance settles to the bottom. About 163 cubic yards of sediment results each day. The thinner sediment is conducted onto an island, where it flows into trenches, and during the winter months the sediment from these trenches is taken to a point down the river Moldau, where it is again placed in open trenches to evaporate, when it is sold as fertilizer. It is taken down the river in closed tanks on open boats. After removing all the solid substances the water remaining runs into the river. Kitchen sinks and water closets are connected with the sewers. The street washings flow into the same sewers. Practically the entire city is provided with sewers for household waste. There has not been any other method of treatment. Street sweepings, garbage, and ashes are hauled to depositories in the suburbs and sold to farmers.

RUSSIA.

Modern Methods of Sewage Disposal in Moscow.—The city of Moscow has a population of about 1,580,000, and about 40 per cent of the city is provided with sewers for household wastes. A separate system of canalization is provided to carry off the street washings. The sewage is filtered on sewage fields and part of it is subjected to biological treatment on the city station. The sewage fields are giving very good results. The waters, after passing several filters, are

used to irrigate plantations of cabbage and other vegetables, which find a ready sale in the city. The city is still making experiments with the biological purification of the sewage.

Sewage Disposal in Odessa.—The sewage of the city of Odessa, population 520,000, is to a large extent used on irrigation fields, where it gives excellent results. Good crops of vegetables are obtained and fair results have been obtained with wheat. The street sweeping, garbage, and ashes are dumped outside the city, although a small proportion is destroyed in a destructor.

STANDARDIZATION OF PUBLIC UTILITIES SERVICE.*

Dr. E. B. Rosa, Chief Physicist United States Bureau of Standards, in an address before the American Association for the Advancement of Science, on "Standardization of Public Utilities Service," discussed the relation of the Bureau of Standards to public utilities and public service commissions. He said that an important work may be done in standardizing public utility service, not with a view of requiring all companies to conform to one standard, but to have standards, adapted to different conditions, that can be used to judge the performance of any utility.

Obviously, no state commission could undertake to establish such standards of efficiency and performance for all utilities, neither can it be expected that the utility companies themselves will ever formulate such standards. The only practicable way is by co-operation between the commissions and the utilities of the whole country, and the best way of securing such co-operation is for the Federal government to assist. The Federal government, through the Agricultural Department, the Geological Survey, the Bureau of Mines, the Public Health Service, the Bureau of Education and other bureaus and departments, is co-operating with the states in many important lines of work, and such work is undertaken, not because the states cannot do it, but because the Federal government can do parts of it much better than the states.

The Bureau of Standards has been co-operating to some extent with state commissions and utility companies in the standardization of practice and service, but the limited resources of the bureau have permitted only a limited activity. The need of more extended work of this kind has been so generally felt that the Secretary of Commerce has asked for a larger appropriation, and the National Association of State Commissioners, and individual commissions as well, have expressed the hope that the appropriation will be granted.

The bureau would then be able to maintain a staff of engineers and experts to carry on investigations. It could serve as technical adviser to the state commissions if they chose to avail themselves of its serv-

ices, and it would also act as a court of appeals in technical questions. It would, of course, have no legal jurisdiction over any utility, and so would not infringe upon the prerogatives of the state commissions, but the influence of its opinion might be of some value to a commission when the public was expecting the impossible, or a utility was demanding too much, or to a utility that was required by order or by ordinance to do what was unreasonable.

It appears certain that a large activity of the bureau in the field of public utility regulation, studying the problems coming before state commissions and municipal regulating bodies open-mindedly and yet conservatively; serving as a clearing house of information as well as an agency for investigation and the formulation of results for general use, would be productive of results that would more than justify the cost.

Many state commissions have abundant authority, but very limited funds to provide an engineering staff. Appraisal and inspection are expensive, and the states will have to grant considerable sums for this, even if the Federal government co-operates to the extent proposed. State commissions, with large appropriations and engineering staffs, will require a minimum of assistance; but most of the states, at least at the start, find need of such help.

The consideration of rates may be divided into two parts: First, what average rates must be charged to provide sufficient revenue to pay expenses, provide for maintenance and depreciation, set aside something for surplus or sinking fund, and pay necessary dividends. Second, how shall these charges be distributed among the different classes of customers for the different grades of service; in other words, what scale of charges is equitable, supposing the total necessary income or average charge for service has already been fixed.

To illustrate, in some places where the charge for electrical energy is 10 cents per kilowatt hour to the ordinary small user of energy, the prices are scaled down as the quantity and load factor are increased (and according to the effect of the load on the station's diversity factor) until it is sometimes as low as 1 cent per kilowatt hour. On the other hand, the price of gas to different customers seldom varies by so great a ratio as 2 to 1, and often the rate is the same to all, regardless of quantity or cost of delivery. There are good reasons why the difference should be less for gas than for electricity, but the practice should not vary as much as it does in different places either in gas or electric rates.

Much study has been given to rates, but there is still much difference of opinion on both theory and practice. Rates are fixed with regard to other considerations than the cost of the service, and the evaluation of such considerations as well as of the cost is difficult indeed. How to distinguish between what is proper and improper is the main question. It is of

*From American Gas Light Journal.

great importance that the state commissions co-operate in the study of the problem, and the utility companies should welcome such study.

To suggest that it is too delicate to be discussed in the open creates the suspicion that there is something to conceal. When there is adequate regulation such a study would be made from the standpoint that whatever hurts the utility company hurts the public, and rates that permit the company to build up its business enable it to give better service to all its customers. In other words, where regulation is adequate and just, the interests of the utility and of the public are one; rates which are just and equitable will contribute to the maximum development of the business.

Public utilities are not regarded as entitled to charge all the traffic will bear, or to make all the money they can. They are now considered as of a public character, enjoying a monopoly, but owing a duty to the public, are entitled to only a fair return on their investment. If a city wishes to own its utilities it may not build new, and disregard the rights of the companies, but must purchase the properties at fair valuations. Neither should a city grant a franchise to a competing company, for one company with all the business can usually render better service than two with the business divided between them.

Thus the utility company is guaranteed a monopoly of the business, protection of its capital and a fair rate of return. It in turn is expected to render the best service possible for the charges made. To secure good service and good management, competent operators must be employed, and the rates must be high enough to permit paying good salaries and good wages. In short, the public pays all the expenses of operating the utilities, and the waste due to inefficient management, if there be such, and the expenses of the commission which regulates the utilities.

It is, therefore, no wonder that there is a public demand for competent regulation of public utilities by commissions, such regulation comprehending rules specifying the service that shall be rendered and fixing rates to be charged, and including effective inspection to see that the management is competent and efficient.

It may appear to some that a commission is going beyond its proper sphere when it inquires into efficiency of management and honesty of administration. But if it be conceded that the stockholders are to receive a fair return on their investment, and the public is to get no better service than the company can give consistently with its rates, any loss due to inefficiency of apparatus or incompetent management comes out of the public rather than from the officers or stockholders.

Such regulation corresponds with the view that "the fundamental relationship between the public and its public utilities is that of principal and agent." But it will require years to develop such regulation to a state approximating completeness and perfection.

The principal elements which determine the value of service are quality and quantity, and in some cases the time and rate of delivery. The quantity may be measured by meters or by count or time, or by the distance traveled. It is comparatively easy to measure quantity of service, although vigilance is needed to insure satisfactory meter accuracy, but to specify the quality of service and to determine what is good service and to ascertain whether the quality of service specified is actually rendered, are much more difficult matters.

There is no absolute standard of quality. In general, the better the service the more it costs, although the difference in cost between good and indifferent service is not the same under all circumstances. Aside from difference in quality of service, due to different conditions, it is difficult enough to specify what constitutes safe and adequate service under average conditions.

For gas service it has been done more or less successfully for many years, and in many cities gas inspectors make systematic tests to ascertain whether the service specified is being furnished. The Bureau of Standards has made an extended study of the subject of specifications for manufactured gas and gas service, and a detailed report on the subject has been published. But no corresponding publication has been issued for electric service, although there should be such.

Whether a manager is spending the stockholders' or the public's money, it is very desirable that as definite service specifications as possible be formulated for his guidance both in the equipment and in the operation of his plant.

This does not mean that such rules need be carried to unnecessary extremes, but that, in a careful and conservative way, and with the co-operation of the utility companies, rules be prepared which are both reasonable and progressive. In other words, they may be largely self-regulating, just as other corporations may obey the law voluntarily, if it is sufficiently clear and explicit so that it can be readily understood. For the information of the public it is important to have such specifications, that it may be generally known what the companies are expected to do.

Managers of utilities can report their performance to the municipalities or public service commissions, and they can receive public credit for good performance as well as criticism for poor performance. In short, it seems as necessary for the public utilities to be standardized as to service and efficiency and to have regulations or specifications adopted for each class of utilities as it is to have specifications written to accompany contracts for other kinds of service.

To make clear why the Bureau of Standards is the proper agency to undertake this work it is desirable to explain briefly what the bureau is, and to give some examples of work that it has done.

The bureau is a national standardizing and research institution, working chiefly in the fields of physics and chemistry, and of electrical, mechanical and civil engineering. Foods and drugs, as known, are studied and tested by the Bureau of Chemistry of the Agricultural Department; geological problems by the Geological Survey; the problems of mining and the economic treatment of minerals by the Bureau of Mines; meteorological problems and weather prediction by the Weather Bureau, and a score of other bureaus have their various fields of activity. The bureau is investigating and testing many of the instruments used by the public utility companies, and it has an unrivalled equipment for such work. It has also investigated some of the problems of the utility companies and has an organization ready to take up further work as soon as the funds are provided.

The Bureau of Standards always seeks information at first hand, and in studying utility problems it works in the fields as well as in the laboratory, and freely consults those having valuable experience. As a national bureau it has the advantage of getting information from all parts of the country and from all classes of engineers and operators. Its engineers and experts are unbiased and absolutely independent, so there is less likelihood of prejudice from personal interest or preconceived notions than if the investigations were of a local character.

One phase of gas manufacture that has received considerable attention is the most economical heating value for different kinds of gas. At the present time the bureau is making a study with reference to gas made from crude petroleum on the Pacific Coast, which study is undertaken at the request of the Public Service Commissions of Oregon and California and a committee of the gas companies of the coast. The results of this study will be utilized by the state commissions in fixing the requirements of their respective states.

An extended study has been made of the damage caused to gas and water pipes, lead cable sheaths and reinforced concrete by the electric currents of street railways, and of methods of preventing such damage, and very valuable results have been obtained. The handling of this subject by public service commissions is perhaps not expressly authorized by law; but as it is a case of the electric current used by one utility destroying the property of others it is of concern to these commissions, and the methods employed by the bureau are applicable generally.

The annual report of the Illinois State Mining Board for the fiscal year ending June 30, 1913. Board for the fiscal year ending June 30, 1913, shows that the total production of coal for the year was livered to the railroads for shipment. The year showed an increase over the previous year of 4,418,721 tons of coal mined. Four hundred and forty-eight more men were employed.

COLLOIDS AND CRYSTALS, THE TWO WORLDS OF MATTER.*

By ROBERT H. BRADBURY.†

When a solid is brought into contact with a liquid the result depends upon the nature of both. There may be apparently an entire absence of interaction, as when rosin is shaken up with water or chalk with alcohol. Or, as when sugar is agitated with water, the solid may disappear, entering into solution in the liquid. The study of sugar solution shows quite clearly that the connection of the sugar molecules with each other has been completely destroyed. They are dispersed through the water very much as the molecules of a gas distribute themselves uniformly in a vacant space, and in both cases the permanence of the uniform dispersion is due to the incessant motion of the molecules. Were the molecules at rest, both the sugar and the gas would settle and form a layer on the bottom of the containing vessel.

However, the molecules of the sugar retain their structure intact, the action being limited to their dispersion. When salt, on the other hand, is dissolved in water, a further breakdown occurs, the molecule is separated and ions of sodium and of chlorine move about in the liquid. Both solutions freeze below 0° C. and boil above 100° C. The most important difference between them is that the salt solution conducts the electric current, while the sugar solution is as poor a conductor as water itself.

A fourth possibility presents itself when glue or gelatin is treated with water. The gelatin absorbs water, swells up and, under the influence of heat, dissolves, but the liquid freezes and boils at practically the same temperatures as pure water. The study of the solution shows that the dispersion is not molecular. The particles of gelatin in it are composed of variable and rather large numbers of molecules. A system like this gelatin solution which presents a case of very fine but not molecular subdivision is called a *colloidal solution*. There are certain solids such as gelatin and dextrin (with water), and rubber (with benzene and carbon disulphide), which, when they dissolve in liquids, are invariably dispersed in this way. Such solids may properly be referred to as *colloids*. They are all amorphous. Crystallized substances never yield colloidal solutions by mere spontaneous solution in a liquid. They always produce molecular or ionic dispersions. However, the phenomenon of colloidal solution is perfectly general, and crystallized substances can also be obtained in this condition, but not by mere solution.

It is an interesting fact that a substance which yields a colloidal solution with one solvent may form an ordinary molecular solution with another. Soap is an example. Its concentrated solution in water boils at about 100° , freezes at about 0° , and exhibits the

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behavior of a colloidal solution in general. On the contrary, a soap solution in alcohol shows the normal change in freezing and boiling points corresponding to the molecular weight, and conducts itself in all respects like an ordinary molecular dispersion.

Every one is familiar with the distinctions between solutions and suspensions. Suspensions are turbid in aspect, and the solid can be removed by letting it settle, or by filtration. Solutions are clear, dissolved matter does not subside and is unaffected by filtering. Colloidal solutions occupy an intermediate position.

Consider for a moment the effect of increasing subdivision on a suspension of finely-divided gold in water. So long as the diameter of the particles is much greater than a thousandth of a millimetre,¹ the system will be turbid and the gold will settle rapidly. But the wave-length of visible light ranges between 0.4μ and 0.7μ , and when the particles become smaller than this they can no longer reflect light and the liquid will appear clear. At the same time there will be a rapid falling off in the speed of settling. Stokes has derived a formula for the velocity of subsidence, I' , of small spheres of radius R and density S falling in a liquid of density S' and internal friction f under the force of gravity g :

$$I' = \frac{2}{9} g (S - S') \frac{R^2}{f}$$

Substituting the proper value for gold and water and assuming a radius of μ for the particles, the value for I' is about 14 centimetres per hour. This means, of course, that the system would be a coarse suspension and would clear up at once. But when $R = 10 \mu$, I' is only about a centimetre a month. This begins already to be fairly permanent. It must be remembered that the high density of gold (19.5) increases the rapidity of subsidence. If we make the calculation for $S = 3$, which is about the density of arsenious sulphide, I' comes out only about a millimetre a month.

So much for calculation. Now what are the facts. As a matter of fact, the dispersed substance in a colloidal solution does not settle at all, so long as the subdivision is maintained. Colloidal gold solutions have been preserved unchanged for years. I have a solution of arsenious sulphide which has remained apparently unchanged for three years and whose countless particles can readily be seen, engaged in their incessant Brownian movement, with an ordinary oil immersion lens. Whenever settling does occur, it is preceded by the aggregation of the particles into larger particles, which finally attain a diameter of μ or over, and slowly subside.

Here, then, is an apparent discrepancy between Stokes' law and the facts. The law informs us that the speed of subsidence decreases rapidly with de-

creasing radius of the particles, but it does not lead us to expect the total absence of settling which presents itself when the average radius is 10μ or thereabout.

The explanation, of course, is molecular motion, or, in other words, *heat*. The particles are battered, on all sides, by a hail-storm of molecular impacts. If the particle is large, the blows of the molecules of the solvent in different directions neutralize each other. But when the particle is not so very much larger than the molecules themselves a molecule striking, say on the left, will give the particle a very perceptible push toward the right, "just as a cork follows better than a large ship the motion of the waves of the sea."² As the dimensions of the particle approach the molecular dimensions it begins to behave like a molecule and is swept along in the endless molecular movement. The cause which prevents the particles in a colloidal solution from settling is in no way different from the cause which prevents the earth's atmosphere from subsiding to a snowy layer a few feet deep on the surface of the planet.

It is worth remembering, also, that the particles of the dispersed phase ordinarily possess an electric charge, which is usually negative. The effect of the repulsion of these similar charges would be to preserve the distribution of the particles throughout the liquid. It is a fact that, when the charges are removed, the system becomes instable and subsidence—preceded by coalescence of the small particles—readily, but not necessarily, occurs.

On the subject of the classification of colloid systems we must be very brief. One proposal subdivides them into *suspensoids*, such as the sols³ of gold and arsenious sulphide, in which the dispersed phase is solid, and *emulsoids*, in which the dispersed phase is liquid. This classification would appear to be an attempt to extend the familiar distinction between liquid and solid to a domain in which that distinction has little if any meaning. To assert that a thing is solid is to say that it has a definite shape, which it retains with some persistence. There is not the slightest reason to think that the particles in a gold sol are solid. It is usual to assume that they are spherical, but this is done merely because it is the simplest assumption to make. There are faint indications that they really have the form of leaflets or of little rods, but they appear in the ultra-microscope simply as brilliant dancing points, and in reality we know nothing whatever about their shape. In connection with this it is interesting to recall the fact that the formation of a crystal begins with the appearance of minute liquid spheres (globulites),⁴ which pass through several stages (margarites, longulites, etc.) before the crystal is formed.

² Perrin.

³ Thomas Graham introduced the term sol as an abbreviation for colloidal solution.

⁴ Fink, "Poggendorff's Annalen," vol. 46, p. 258 (1839); Schmidt, "Liebig's Annalen der Chemie," vol. 53, p. 171 (1845); Frankenheim, "Poggendorff's Annalen," vol. III, p. 1 (1860).

¹ It is usual to employ the symbol μ (the Greek letter mu) for the thousandth of a millimetre. In the same way, $m \mu$ indicates the millionth of a millimetre.

It seems possible that, under such enormous subdivision, cohesion retires into the background and surface tension assumes the chief role, so that the gold particles are rather to be compared to minute drops than to little crystals.

Enough has been said to make clear the uncertainty which attaches to the attempt to classify colloid solutions according to the state of aggregation of the particles. A better classification is into *reversible* and *irreversible* colloids, according to the way in which the dissolved substance behaves when separated from the solution. Thus, when a gelatin solution is evaporated until it "sets" it is only necessary to warm the jelly with water to obtain it again in colloid solution. Gelatin is a typical reversible colloid. But when the gold is caused to separate from a gold sol—which can easily be brought about by adding any electrolyte to the sol—the gold will not again enter into colloidal solution. Shaking or warming with water gives a mere suspension, which settles at once. Gold is an *irreversible* colloid. The distinction is fundamental. Many organic colloids are reversible, while it is rather the habit of the inorganic colloids to behave in the irreversible way.

In order to prepare a sol containing an irreversible colloid all that is necessary is to reduce the solid to extreme subdivision in a liquid in which it is insoluble. The electric arc furnishes a rapid and simple method.⁵ Two gold wires about 2 mm. thick are connected with a 220-volt circuit and brought together under distilled water. A 110-volt circuit can be used, but more patience is required. Sols of platinum, silver, copper, and other metals can be made in the same way. By related electrical methods, using such liquids as pentane and anhydrous ether, Svedberg⁶ obtained sols of all five of the alkali metals. The colors of the sols agreed with those of the vapors of the corresponding metals.

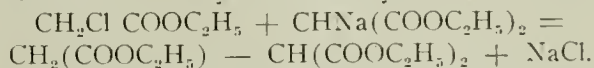
Chemical reduction of a salt of a metal furnishes another method which has been largely employed by Zsigmondy⁷ and other investigators. For instance, a very dilute solution of auric chloride is mixed with such reducing agents as formaldehyde, hydroxylamine or an ethereal solution of phosphorus. The gold sols obtained in this way are usually red by transmitted light, the particles being bright green and very much smaller than in the sols obtained by the electrical method.

By various chemical methods, which lack of space forbids us to discuss, sols of sulphides (CdS , As_2S_3 , Sb_2S_3 , etc.) and oxides (Fe_2O_3 , Al_2O_3) can be obtained. The sol of aluminum oxide is important on account of its connection with dyeing and mordanting. The formation of the blood-red sol of ferric oxide by adding a concentrated solution of ferric chloride to

about 50 volumes of boiling distilled water is a simple and beautiful lecture experiment.

In making colloidal solutions of *salts*, the essential thing is to mix dilute solutions of the precipitants, using a liquid in which the insolubility of the product is as complete as possible. Thus, in mixing very dilute solutions of sodium sulphate and barium chloride, a crystalline precipitate is usually obtained. The reason is that barium sulphate possesses a very slight but real solubility in water. Hence the liquid in contact with the particles first formed contains enough barium sulphate to nourish their growth and allow them to develop to crystals. If alcohol is added to the sulphate, before the barium chloride is introduced, the solubility of the barium sulphate is greatly reduced, and it is obtained in colloidal solution without difficulty.

In the same way, if we mix water solutions of sodium hydroxide and of hydrochloric acid we obtain merely an ordinary solution of common salt. But if salt is produced by reaction between organic compounds in a liquid in which the sodium chloride is insoluble, then a colloidal solution is obtained. For instance, when chlor-acetic ester interacts with sodium malonic ester, a grayish opalescent sol of sodium chloride in ethenyl tri-carboxylic ester results.



At low temperatures, in such liquids as toluene and chloroform, even *ice* has been obtained in colloidal solution.

The most striking property of the reversible colloids is that they are able to communicate their reversibility to the irreversible ones. Thus, if a trace of gelatin is added to a gold solution, the gold becomes much more difficult to coagulate by electrolytes, and when coagulated it can be dispersed again by merely warming with water. This curious protective action is exerted, in greatly varying degree, by most reversible colloids. Direct study of the phenomenon with the ultra-microscope shows that the view frequently expressed that the gelatin envelops or forms a film around the gold particles is incorrect. What actually happens seems to be a direct combination between gelatin particles and gold particles, which then pass through the reversible changes together.

Protective colloids enjoy a wide practical application. In the manufacture of photographic films the gelatin retards the crystallization of the silver bromide. Ink often contains a colloid which prevents the pigment from settling. The lubricant "aqua dag" put in the market by the Acheson Co. consists of finely-divided artificial graphite, held up by a protective colloid. Clay is made plastic for the potter by an empirical process which involves the action of protective colloids derived from decaying vegetable matter. The addition of gelatin in making ice cream depends upon its protective action in preventing the growth of ice crystals, which would make the product

⁵ Bredig, *Zeitschrift für Angewandte Chemie*, 1898, p. 951. For a full account of Bredig's work with the platinum sol, see *Zeitschrift für physikalische Chemie*, vol. 31, pp. 258-353 (1899).

⁶ *Berichte der Deutschen Chemischen Gesellschaft*, vol. 38, p. 3616 (1905).

⁷ See his monograph, "Zur Erkenntnis der Kolloide" (Jena, 1905), which has been translated by Jerome Alexander.

"gritty." Without doubt protective action plays an important role in the cleansing action of soap. This has been made clear by some recent experiments of Spring.⁸ Lampblack, freed from oil by long washing with alcohol, ether, and benzene, forms a rather stable suspension in water, but the lampblack is detained by a paper filter. If the filter is now reversed, so that the blackened surface is outward, and water poured through it, the lampblack is not removed, but a dilute soap solution removes the coating and cleanses the filter at once. Finally, lampblack suspended—or colloiddally dissolved—in soap solution, passes through a filter unchanged. It is of much practical interest that there is a well-marked optimum in the concentration of the soap required to protect the lampblack. A one per cent soap solution is the most efficient. In two per cent soap solution lampblack sinks about as rapidly as in pure water.

We have already considered the probable actual condition of the particles in a colloidal solution and have concluded that, for the present, no very definite information is obtainable about the matter. We must now return, for a moment, to the subject in order to allude to the thesis so brilliantly advocated by van Weimarn, the Russian investigator, who holds that the particles are of necessity minute crystals and that there is, in fact, no such thing as amorphous matter. He even goes so far as to state the substances like air and water are in a "dynamic crypto-crystalline condition," though I have been unable to understand what he means by this statement.

Briefly, the evidence that van Weimarn adduces to the support of his hypothesis is:

(1) That colloid particles will grow to crystals if provided with the proper nourishment, namely, a dilute solution of the same substance.

(2) That colloid particles are capable, when introduced into a supersaturated solution of the same substance, of discharging the supersaturation and inducing the formation of crystals.

Those who desire to follow this matter further should read van Weimarn's little book, "Grundzüge der Dispersoidchemie," after which they will find themselves very much interested, but somewhat unconvinced. Let me hasten to add that I have not the least desire to undervalue the brilliant experimental work of the Russian chemist. It is, in fact, precisely by the conception of more or less daring hypotheses, and the working out of their consequences, that our science achieves its endless victory over the nescience about us.

We have seen that the wave-lengths of the visible radiations are comprised between 0.4μ and 0.7μ . With objects much smaller, the ordinary microscopic method ceases to be applicable. Using ultra-violet radiation for illumination, quartz lenses in the micro-

scope, and receiving the image with the photographic plate instead of the eye, it is possible to advance a step further in the domain of the infinitesimal, but only a step, and there are obvious objections to the proceeding. Since some of the particles in colloidal solutions are only 0.006μ in diameter, we can never hope to see them as little bodies subtending a visual angle. The *ultra-microscope*—the powerful instrument of investigation to which most of our knowledge of colloid systems is due—renounces this idea and makes the particles visible merely as glittering points on a black background. The sol is placed in a small rectangular glass trough and a horizontal beam of arc light or sunlight focussed in it. The microscope is placed vertically above the trough. It will at once be seen that there are two fundamental things about the instrument: to provide intense illumination, and to make sure that no light enters the microscope except the rays which emanate from the particles. The principle is simple, but the system of diaphragms and lenses needed to secure the second object makes the ultra-microscope an elaborate and expensive instrument in practice.

Cotton and Mouton⁹ achieve the same end in a different way. The illumination (arc or sunlight) is thrown up from below by a paraboloid reflector so ground that all rays, *except those diffracted by the particles*, are totally reflected from the cover-glass over the sol. This instrument is simple, easily adjusted and cheap. It is made commercially by the firm of Zeiss. It would seem to be admirably adapted to school purposes. In fact, after a look into the ultra-microscope, the study of the molecular topics ceases to be drudgery and becomes a positive intellectual need.

Even a brief glance at the subject of colloid systems must at least mention the classic work of Perrin¹⁰ on the distribution of the particles in suspensions of gamboge and mastic. He succeeded, by an ingenious and simple method, in preparing emulsions of gamboge in water in which the spherical yellow granules were all of the same diameter. If we consider a mass of such a liquid in a tube, it is clear that the granules, if at rest, would, since they are denser than water, all fall to the bottom. The fact that they remain suspended is due to their movement. In other words, the state of things is the same as in the earth's atmosphere, and just as the molecules are more crowded near the earth's surface, so the granules of gamboge must be more numerous near the bottom of the liquid than in the upper layers. Perrin verified this prediction by direct counting of the granules under the microscope. The barometric formula which describes the progressive rarefaction of air with increasing height also

⁹ Compt. Rendus, vol. 136, p. 1657 (1903).

¹⁰ Annales de Chimie et de Physique, 3d Series, vol. 18, p. 5 (1909). There is a German translation by Donau in Kolloid-chemische Beihefte, vol. 1, p. 1 (1910). An English translation by Soddy has appeared in book form under the title, "The Brownian Movement and Molecular Reality."

⁸ Kolloid Zeitschrift, vol. 4, p. 161 (1909); Kolloid Zeitschrift, vol. 6, pp. 11, 109, 164 (1910).

describes the distribution of the granules in Perrin's uniform emulsions. The only difference is that, while the aviator must ascend six kilometers in order to reach air half as dense as at sea level, the same effect is produced, in Perrin's emulsion, by an ascent of 0.1 millimeter.

That the mean energy of rotation of a molecule must be equal to its mean energy of translation is one of the chief propositions of the kinetic theory. Perrin has proved this by direct measurement of the rotation of granules under the microscope. For this purpose, large granules (15μ) of mastic were employed. These are far too heavy to remain suspended in water, so a solution of urea was used. Fortunately, the granules contain little inclusions which make it possible to measure their rotation.

These are only two of many fundamental results contained in this wonderful memoir. Van't Hoff extended the gas laws to solutions. Perrin has now proved them to be valid for systems in which the moving particles are visible realities. Let us end by quoting one of the sentences of his conclusion:

"La découverte de telles relations marque le point où s'élève, dans notre conscience scientifique, la réalité moléculaire sous-jacente."

INSPECTION OF GOVERNMENT COAL PURCHASES.*

The inspection of coal purchased for the Government is conducted from the headquarters of the bureau in Washington, where the engineer in charge of the inspection service is stationed and the laboratory for analyzing samples of deliveries is situated.

The work done includes the collecting, analyzing, and testing of samples representing deliveries of coal purchased under Government contracts providing for purchase on a specification basis, in order to ascertain whether the coal represented by the samples conforms to the stipulations of the contracts. On such contracts the bidders guarantee the quality of the coal they offer, and the quality guaranteed by the successful bidder becomes the standard of his contract. A large part of the coal used by the Government for its power plants, public buildings, and naval stations is purchased under contracts that specify the ash and the moisture content, the heating value, the limits of the content of volatile matter, and the sulphur content. The analysis of samples of deliveries determines whether the quality of the coal is up to the standards guaranteed by the contractor. If it is not, the price to be paid is decreased in proportion to the lower value of the coal; if the coal is of higher quality, the price is proportionately increased.

In the collection of samples a definite scheme of procedure is observed. By following the instructions of the Bureau of Mines and by observing every practicable precaution, the collection of samples fairly rep-

resenting the coal delivered is insured. The gross samples taken are reduced by successive crushings, mixings, and partings to samples that weigh about three pounds. These are sent by mail to the laboratory in Washington.

The larger part of the coal now bought by the Government is purchased under the general technical supervision of the Bureau of Mines. The cost of purchases under specifications prepared by the bureau for the use of the Government now aggregates approximately \$4,500,000 per annum, and the additional fuel bought under the general advice of the bureau now aggregates in purchase cost some \$3,000,000 per annum more, making a total value not less than \$7,500,000.

The benefits to the Government from this work of the bureau have been both general and special. In the case of the purchase of coal by the Isthmian Canal Commission for the Panama Railroad during the fiscal year 1910 and 1911, the money actually saved by the Government was nearly \$75,000 and the real saving was probably several times these figures, because the method of purchase insured deliveries of coal of a higher grade than would otherwise have been obtained. Other examples might be mentioned, among them the saving effected by the Quartermaster Corps, War Department, which amounted to \$27,500 during the fiscal year 1912.

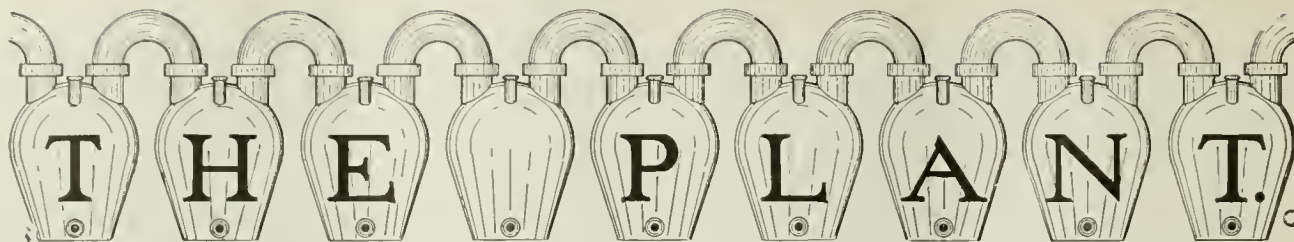
Some benefits to the general public resulting from this work for the Government may be indicated by the fact that more than fifty of the larger cities, a number of states, and a large number of private corporations and business concerns in different parts of the country have followed the general plans adopted by the Government for the purchase of its coal.

The analyses of coals from the different coal fields of the country, analyses that have been made in testing these coals for the use of the Government, have been of great service to engineers in charge of power plants and to manufacturing industries throughout the country, enabling users of fuel to determine in advance the character of the coals available for local or special use.

The specification method of purchase protects the Government against the delivery of poorer coal than that guaranteed by the contractor and incites dealers to prepare the coal more carefully.

In the case of coal for use on naval vessels, at the request of the Navy Department the mining and shipping facilities of mines from which purchase is proposed are carefully examined by the engineers of the Bureau of Mines, and the samples collected from each mine are analyzed at the Pittsburgh laboratory; in this way a standard of high-grade coal, low in ash and volatile matter, is fixed, and must be maintained in subsequent shipments. Occasionally samples are collected as the coal is being loaded on ships, and if the results show that the coal as loaded is not up to the standard, the contractor is promptly notified.

*From the Forthcoming Third Annual Report of the National Bureau of Mines, Joseph A. Holmes, Director.



THE PRESENT STATUS OF THE WOOD TURPENTINE INDUSTRY*

By E. H. FRENCH and JAMES R. WITHROW.

In treating a subject that has as many phases as this one, it will be necessary to discuss briefly an allied industry, namely, that of gum turpentine as distinguished from wood turpentine, in order that the reasons calling for the development of this latter industry may be seen with the proper perspective.

That the wood turpentine industry is at present at an extremely low ebb is unquestionably true. Nevertheless, it is likewise true that its scientific development is an economic necessity for certain localities, in order that waste may be conserved, that the products from waste replace those from the fast disappearing pine and fir forests and that cut-over land may be cleared at a profit instead of at a loss. Therefore, in this instance, as is often the case, necessity compels development.

The fact that thousands of dollars have been expended and lost in the incubation of this industry has been due, in our opinion to three main causes, any one of which in itself would account for failure: first, the lack of practical scientific engineers experienced in this or analogous fields, and second, financing for the sale of stock and securities rather than product, and third, lack of efficient marketing organization. It must also be borne in mind, that owing to the number of different processes, there was caused a lack of uniformity of product, which naturally tended to increase selling costs. Except to the U. S. Navy, little, if any, wood turpentine has been sold on thorough specifications. There has as yet been no real attempt by manufacturers to effect a general standard, although a few years ago the producers of the practically defunct steam process turpentine, did make an attempt to standardize their product.

One of the important influences that tended at first toward the development of the industry and later proved extremely detrimental, was the speculative nature of the naval stores market. This was made up entirely of gum turpentine and rosin, upon the prices of which the relative wood turpentine values were determined. This market in the past has been subject to violent price changes, a fluctuation of from 30c to over \$1.00 per gallon having been experienced, and this was due almost wholly to speculation. Naturally therefore, during the upward swing of prices an un-

natural development occurred and plants using costly processes and with inefficient management were profitably operated and exploited. It followed, of course, that when the national government, through criminal prosecution, put a stop to excessive speculation, a corresponding reaction occurred ruining many concerns which required abnormal prices for financial success.

Unreasonably high prices not only encouraged the development of the wood turpentine industry, but also caused an expansion in operations by the gum turpentine manufacturers so that a larger percentage of trees, and many very young trees, were boxed, causing over-production.

GUM TURPENTINE.

The method of producing oil of turpentine from the resins of coniferous trees, consists in cutting a broad wedged-shaped notch or cup at the base of the tree and removing the bark immediately above the notch for about 18 to 24 inches. The resin exuding from the peeled area runs into the cup at the bottom and is collected from time to time. Each succeeding season the barked area is increased until it reaches about the height of one's head, usually taking five or six years. As many as four "boxes" are thus cut on one tree, depending on its size, permitting only enough of the original bark to remain to prevent the death of the tree.

After collecting sufficient quantity of the resin, it is distilled in a copper still, usually a "fire still," equipped with a live steam jet or a water supply. The turpentine thus produced is not carried farther in any refining process, but is ready for the market. The residue in the still is the rosin of commerce and is barreled at the still. The dross obtained by filtering sticks, dirt, etc., from the rosin is in many places being worked into the cheaper grades of rosin. With rosin at an average price, it is generally figured that to make the operation profitable, about 42 cts. per gallon must be obtained for the turpentine.

The marketing of the products is done through "factors" as they are called, that is, companies or individuals who contract with the producers for their output, supply them with funds for pay rolls, etc., and advances when necessary. These "factors" take the product when produced, but usually have no other connection with the producer. Savannah, Ga., is the leading naval stores center in the world and usually Savannah prices are accepted as the standard. Jacksonville and Pensacola, Fla.; Brunswick, Ga., and New Orleans, La., are also large "factor" centers for this industry.

*Paper read before the New York meeting, American Institute of Chemical Engineers.

This method of producing turpentine is generally conceded to give the best turpentine and rosin, but unless more scientific methods are very widely adopted, the time is fast coming when it will be necessary to supply these products from another source, for present methods of operation are coming to be looked upon as directly antagonistic to all ideas of conservation under American lumbering conditions, as they so weaken the trees that the loss from windfalls is extremely large. In fact, many large lumber companies have given up "boxing" for this reason, and also because they feel that the growth of the young tree is retarded.

Modifications of the old "boxing" methods are being used in some places. Metal cups are substituted for the box cut in the base of the tree, and light chipping is being tried. It is claimed that the loss from windfalls is considerably reduced by some of these modern improvements. At least one large southern lumber company is at present experimenting on 5,000 acre units in order to determine definitely, if possible, the merits of these new cups and other modifications as to yield and influence on windfalls, and also to decide the effect "boxing" may have on finished lumber.

WOOD TURPENTINE.

Wood turpentine came into commercial notice about the year 1900. The name was, and is, applied to the product obtained from dead and down timber, a waste product called "lightwood." The live or green wood is not so suitable for this manufacture owing to the moisture content and also to the fact that the bark still remains. Stumps, however, are very valuable, as they contain a much larger proportion of resins than "lightwood." Nevertheless, the cost per cord of stump wood is considerably more, as the stumps usually require the additional expense of removal by explosives. The cost per cord of "lightwood" at the works will run from \$2.00 to \$3.00, making, however, no allowance for its value as waste; while stump wood will vary from \$3.50 to \$5.00 per cord, the price depending on acre stumpage and hauling distances. The manufacture may be divided into five processes: steam process, solvent process, alkali process, bath process and distillation process.

Before entering into a description of these various methods we desire to emphasize the statement that the manufacture of wood turpentine necessarily will become of far reaching importance in the future. This is for the reasons that it is utilizing an absolutely waste product and is at the same time clearing cut-over lands and rendering them fit for occupancy. We wish also to emphasize the statement already made that many past failures were due to the unreasonable speculative condition of the markets. Abnormally high prices of naval stores induced promoters and unscrupulous persons to capitalize their concerns on the earning capacity during this period, thereby making them "stock jobbing" propositions rather than legitimate manufacturing institutions. This kind of financing while appar-

ently expanding the industry really retarded development, as the energies of the management were expended primarily in the office and at the expense of the manufacturing organization.

We have seen from time to time, figures of promoters regarding yields and manufacturing costs of the different processes which are not in accord with the results obtained from continuous operation. It may not be entirely without value therefore to cite some comparative yields and operation costs in these different processes. This is especially true since there does not appear to be any published data of this nature. While the records themselves of individual plants, would be interesting, such records are often misleading and in view of actual or possible competition the location of plants must be withheld.

In submitting data as to yields, values, and productive costs, we have compiled them mainly from the actual results obtained during continued operation of a number of large plants. As so many elements making up these figures are variable, owing to location, construction and raw material, our endeavor has been to average them so that a comprehensive idea may be had as to actual results obtained commercially.

Steam Process.—This process was the first to be extensively placed in commercial operation, and is very simple in its construction and handling, consisting merely of "hogging" the wood and placing it in a steel cylinder, usually holding about a cord, distillation being carried on with live steam and under varying pressure. However, there probably was little difference in results whether a maximum of five pounds or twenty pounds pressure was used. Distillation was carried forward until oils cease to be obtained in quantity.

It should be borne in mind that there is a decided variance in the resinous content of wood, therefore, it was quite possible to make a selection that would run as high as 30 gals. of turpentine to the cord. We believe the following figures, however, based on a cord of long leaf yellow pine lightwood, weighing 3,500 lbs., would be the average.

Turpentine, 9½ gals. at 35 cts.....	\$3.32
Pine oil, 3 gals. at 35 cts.....	1.05
Total value of products.....	\$4.37
Production Cost per Cord.	
Wood.....	\$3.00
Labor.....	1.00
Barrels.....	.42
Freight (approximate).....	.20
Selling commission.....	.25
	\$4.87

The fuel cost is only the labor of handling the treated chips. However, there is no allowance made for the office, upkeep, depreciation, insurance, etc. Therefore, it can be seen that the steam process necessarily, in order to be profitable, demands a market price considerably in advance of the present markets.

The price of wood turpentine is always a few cents per gallon under that of gum turpentine. The quality of the product produced by the steam process, however,

is excellent. Our opinion is, nevertheless, that at least 50c per gallon is necessary as a minimum for successful operation.

Solvent Process.—In the early development of this process the wood was subjected to the old steam treatment and subsequently treated with carbon di-sulphide for the recovery of rosin. The loss of solvent rendered it impractical. In the next stage of development the wood was hogged and placed in digesters for the recovery of turpentine and pine oil. Then the solvent (a low grade of gasoline) was added, live steam was applied recovering some turpentine, pine oil and solvent by distillation. This has been improved, subsequently, in some instances by omitting preliminary steaming, adding solvent direct and recovering this with the turpentine and pine oil by live steam in the primary distillation, obtaining rosin alone when the still is drawn. The rosin, however, is soft, and difficulty has been experienced in obtaining a hard product, but this is overcome by subsequent treatment. In either method a considerable loss of solvent is always entailed, varying from 17 to 30 gallons per cord. The approximate yields and operating costs per cord are as follows:

Turpentine, 9½ gals. at 35 cts.....	\$ 3.32
Rosin, 400 lbs. at \$4.00 per 280 lbs.....	5.72
Pine oil, 3 gals at 35 cts.....	1.05

Total value of products.....\$10.09

Production Costs per Cord.

Wood.....	\$ 3.00
Labor.....	2.50
Loss in solvent at 15 cts. (17 gals.).....	2.55
Barrels.....	.42
Rosin barrels.....	.25
Selling costs.....	.50
Freight.....	.75

Total.....\$ 9.97

Again the actual fuel cost in this process is negligible as use is made of the "treated chips." No allowance is made here for insurance, upkeep, overhead and interest charges, refining costs or depreciation; therefore, it is plainly evident that at present market prices, at least until improvement is made in yields or in minimizing costs, there is not sufficient margin for successful operation. However, it is quite possible that by using the "treated chips" for paper pulp manufacture that this process will be made of commercial value. The operation in this case would have to be maintained on an enormous scale in order to supply treated chips for a pulp plant unit of an economic size. A plant using this solvent system and built on a very elaborate scale, was in operation in Southeastern Georgia, and, despite the most advantageous financial backing, was unable to operate profitably on a weakened market, and is now in the hands of receivers. This citation alone probably would not necessarily condemn the process, but as several smaller plants are either in like position or shut down, it indicates the necessity of research or development if ultimate success is to be attained. As with the steam process many claims of higher yields than we have above credited are made by interested

parties, but these claims are still subject to substantiation.

Alkali Process.—This process is essentially one to be applied to the alkali processes for manufacturing paper pulp from resinous woods with the recovery of turpentine and rosin and at the same time improving the quality of the pulp, and promoting ease of manufacture. The process is well covered by patents.

The basis upon which this method rests is the fact that the sodium hydroxid saponifies the resins in the wood and the sodium resinate thus formed may be separated from the spent soda pulp liquor by temperature regulation. The wood is handled in the same manner as in soda pulp manufacture, except that after digestion the spent liquor is cooled for the separation of sodium resinate before this liquor proceeds to the evaporators. This product has been so purified and refined, commercially, as to produce a good quality of paper size. The resinate may if desired be manufactured into rosin by acid treatment, or destructively distilled, obtaining rosin oils. The turpentine is recovered from the digester blow-off during the digestion operation. This process is apparently theoretically sound, but requires the outlay of capital to develop thoroughly the mechanical details. Fifty to seventy thousand dollars were expended in one case to demonstrate its commercial possibilities and some results were obtained. However, the enterprise has not been financially successful and the plant has been dismantled, a fact which may be due to faulty engineering or other causes; and even though the process appears enticing from a theoretical viewpoint the fact remains that the trial was not successful and there is no process of this kind in actual operation. Nevertheless, it is our opinion that eventually it will be of commercial importance and ultimately the combination of the two industries, paper pulp and turpentine-rosin recovery, thus utilizing resinous wood, will be successful. Unusual yields of turpentine are claimed by a Florida plant using an alkali bath but satisfactory arrangements have not yet been made regarding rosin recovery.

Bath Process.—This process must not be confounded with the recently suggested process using a bath or envelope of oil external to the oven for the purpose of heating the same. This external bath process has not been long enough in operation to demonstrate its future and it will be interesting to note if certain fundamental operation difficulties can be overcome.

By bath process we refer to the process commercially so-called which has been in operation for some time and in which the bath is *within the oven* or retort in contact with the wood itself. Three plants using this method have been built, the first in North Carolina, which has been dismantled, the others at Mt. Pleasant, Ga., and Jacksonville, Fla., which have not been successful under low market conditions and both of which have gone into receiver's hands within the last few months.

The process itself was divided into two separate

general operations. First, the recovery of turpentine and oil, or as styled "Sweet Spirits" and subsequently the destructive distillation of the wood itself, although this second operation was not contemplated in the original process.

The operation has a decided advantage over the solvent and steam processes in that it does not require the "hogging" of the wood.

The general construction used in this first operation consists of steel cylinders at Mt. Pleasant and concrete ovens at the Jacksonville plant, each holding five to nine, one to two cord steel cars, similar in construction to those in common use in hardwood distillation, thus each oven holds about nine cords of wood. Placed at the side of the oven is a heater equipped with a large cast iron worm connected to the bottom of the oven. To the rear of the heater is placed a large steel or concrete reservoir connected by cast iron pipe to the top of the oven and also to rotary pumps which in turn are connected to the heater pipes.

The loaded cars are placed in the oven and melted rosin or pitch is run into the reservoir and circulated by the pumps through the heater and the bottom oven connection. This pitch after filling the oven *in contact with the wood*, overflows into the reservoir and is thus continually circulated through the heater and oven, thereby vaporizing the volatile resinous bodies and without dissociating the wood fibre. The turpentine and oil vapors are carried through a "vapor" chamber where the high boiling liquids that are mechanically carried by the vapor are separated, the vapor continuing to an ordinary tubular condenser, where the crude "sweet spirits" are obtained. Afterwards the "sweet spirits" are refined, the products being turpentine, oil and tarry residue. The time required to treat a charge varies in the plants mentioned from seven to ten hours, and the product obtained is of high quality, though not so good as steam process turpentine.

At first sight it would appear that in this process the rosin from the wood treated would gradually increase the volume of the bath and rosin be thus manufactured. The reverse of this, however, is the case, as a serious loss of bath is actually realized. This is in fact a very serious drawback to the process, and is probably due to the formation of volatile rosin oils when the liquid bath encounters the high temperature of the heater. These rosin oils are volatilized and pass into the "crude spirits," and are lost in the refining residue as only from 65 to 70% of the spirit is received as turpentine and pine oil. By proper arrangement this difficulty would have been avoided.

This process is also seriously handicapped by the fuel consumption of the heaters and the heavy upkeep for heater pipes and pumps. Nevertheless, with proper design, operation costs would have been much reduced from that actually experienced.

After refining, the results from this "Sweet process" could be averaged as follows:

Turpentine, 7½ gals. at 35 cts.....	\$2.62
Pine oil, 2½ gals. at 35 cts.....	.87
	\$3.49

After the charge is withdrawn in this first operation the "treated" wood is placed in ovens similar to those used in the hardwood industry and there subjected to destructive distillation. The results obtained here are very important as a good market has been created for these products. An average of from 68 to 70 gallons of oils is obtained, together with a like volume of "acid water," the latter a "waste" although its utilization was accomplished just prior to the receivership of one of the mentioned companies. In addition there remains in the cars approximately 900 pounds of charcoal and there is produced about 10,000 feet of non-condensable gas per cord which is of fuel value.

This crude distillate above mentioned is called "destructive distillate od D. D. Product" to distinguish it from the product derived from the resins, called "sweet spirits." On refining there are obtained the following products per cord:

Tar, 41 gals. at .08.....	\$ 3.28
Light oil, 6.8 gals. at .12.....	.81
Heavy oil, 10 gals. at .12.....	1.20
Charcoal, 36 bushels at .075.....	2.70
From "Sweet Process".....	3.49
Total.....	\$11.48

Costs of Production per Cord.

Wood.....	\$ 3.00
Fuel.....	3.25
Labor.....	2.75
Cooperage.....	1.00
Selling costs.....	.60
Freight (approximate).....	.75

Again it can be seen that this process handled as it has been in the past cannot be operated successfully on a low market, as no allowances have been made for upkeep, insurance, interest charges, refining costs, management or depreciation. Although the loss in bath is partially made up by the pitch obtained, it can be seen from these costs that improvement must be had before this process can exist during low market conditions. It is not to be inferred however, that the principles upon which the process is based are entirely faulty. The reasons for its failure appeared to be lack of knowledge as to the chemical nature of the products and troubles consequent to improper construction and operation. As is common with approaching dissolution, strenuous efforts at improvements were made in this process, and despite well known prior failures, experiments were completed and operation commenced for the utilization of the waste "acid water" just before the closing of one of the plants. The results proved interesting and promised excellent recovery, as the products recovered, including acetate of lime and wood alcohol represented a net gain of well over \$1.50 per cord.

Distillation Process.—As the wood turpentine industry now stands, the destructive distillation process apparently has the best chance of commercial success, as it is not only more simple in construction and operation, but yields more in volume of products. Chemical

and engineering skill, nevertheless, are necessary for this success.

The distillation process may be subdivided into three divisions. First, that division analogous to hardwood distillation. This method in its primary operation is very similar in equipment and design to the usual hardwood distillation plant, the wood being placed in steel cars and run into ovens. The products derived from the resins and those from the dissociated wood are collected together, and separation is made during refining, although some attempt has been made at fractional distillation in this primary stage. This method gives a much inferior grade of turpentine, etc., owing to the commercial difficulty of eliminating the pyroligneous bodies, and the product will not answer to the permanganate test which indicates pyroligneous matter. The tar produced in this operation is usually resinous and for some uses therefore, objectionable.

The second division is merely a modification of this process, the ovens being in duplicate, and distillation for the resinous bodies being carried out in one oven, so designed or "set" that the temperature can be maintained approximately uniform. After the resinous bodies have been obtained the "treated wood" is withdrawn and placed in a second oven and in this oven the distillation is carried at a higher temperature for the destructive distillation of the wood itself.

The third division is that using concrete ovens containing 12-inch heater pipes running the length of the ovens. These ovens have dutch-oven connections and the flue gases travel through these pipes, and it is claimed that temperature regulation is more easily accomplished.

In all these processes the products obtained are the same, except so far as the degree of purity is concerned.

The first distillate, or that from the resins in these methods will run on an average 22 to 24 gallons of "sweet spirits." This on refining will give from 50 to 60 per cent or from 12 to 14 gals. of marketable turpentine and from 9 to 10 per cent of pine oil or from 2 to 2½ gals., and also 100 lbs. of a very resinous pitch.

The destructive products are the same as those from the "bath process" thus it can be seen that the gross total in this operation should be materially higher than in the other processes while the operating expense is very much lower. This, including wood, upkeep and in fact, all expense, should not, under proper design, construction and management run over \$9.00 to the cord.

The particular objection raised against the destructive distillation process is that the products are difficult to market, and this has been true, to a certain extent, in the past, but when it is considered that many of these bodies were new to the trade this condition cannot be wondered at, and at present the marketing is not more difficult than products of other processes, in fact, just now there is an unusual demand for these products.

MARKETS.

It may perhaps, be of interest to call attention to the various developed markets for the D. D. Products, for we all realize that the marketing of products is at least equal in importance to the manufacture; and this industry shows many instances where comparative merit of process and operation was wholly lost by inferior facilities, and on the other hand instances in which unsound operation was maintained for considerable time by a remarkably efficient selling organization. The latter cases while losing ventures to those financially interested, have no doubt succeeded in creating a growing demand for the products as indicated by the prices obtained now for them with many plants closed down. At the time this article is written tar would easily be sold for 12 cts. per gallon as compared to the 8 cts. allowed in the cost data in the article, but which should be considered maximum, as the future, undoubtedly, will increase supplies so as to bring these prices back to a more nearly normal condition. This fact, however, does show that a demand has been created that did not exist prior to the quite recent establishment of plants of this nature. Perhaps this condition is more clearly evidenced in the heavy D. D. oil, for which 22 cts. per gallon is being obtained. The tar demand had in a measure been previously supplied by that known as "kiln tar" made at works using the kiln system for charcoal manufacture from resinous woods.

The product mentioned as D. D. light oil is at present most difficult to market profitably—this is on the market in this form and is used to some extent by manufacturers of disinfectants. However, it has been fractionally distilled and has been used locally as a substitute for gasoline for use in engines, and has proven itself to be more efficient than gasoline. The comparatively small amount of this product makes its use in this manner merely of local interest, but it indicates a real value of the product.

The heavy D. D. oil has been in consistent and increasing demand, particularly in the paint industry and notably for shingle stains, and also for the manufacture of tar oils for which there is a large foreign demand. The necessity of an energetic market agency was in one case well illustrated within the past year with this product. One large concern was offering this product for 5 cts. per gallon, finding it impossible to market, having nearly 100,000 gallons in storage, while at the same time another company was unable to supply its customers at 18 cts. per gallon. Of course the latter considered the purchase from the former but feared future competition, in case, as seemed dangerously probable, the former concern should learn of their customers.

The pitch produced in the distillation process and distinguished from the tar has a firm market demand from ship chandlers and also is sold for uses such as coating silos, rendering them impervious to moisture.

The tar of course, has its established uses with rope

manufacturers as well as with paint producers, while the charcoal consumption, particularly in the south, is very steady both for domestic use and manufacturing. Of the number of suggested specialties based on the use of tars and oils, doubtless a few will ultimately contribute a steady demand for a portion of these products.

COSTS OF INSTALLATION.

The various processes have in most instances exceeded reasonable installation costs. Undoubtedly the same is true in any newly established industry, and more particularly in cases where as pointed out in this one, prices could be obtained that were out of all proportion to production costs.

Entire equipment of a steam process plant should come well within \$750.00 per cord, capacity, while the solvent process complete should be approximately \$2,000.00 per cord, this also should be approximately that of the bath system, while the destructive distillation method ought to be very close to \$1,500.00. In making these general estimates neither working capital nor purchase of timber of stumpage is considered.

CONCLUSION.

When your attention is brought to the fact that the destructive distillation plants alone have been able to survive recent price depression, it is reasonable to conclude that, in the present state of the art, this method has inherent advantages. Nevertheless, in this type of process, there is room for much improvement, particularly in refining and the utilization of waste products ignored in the past. Constructive chemical engineering apparently has in this industry, opportunity to create an unusually profitable business, provided it utilizes the unfortunate mistakes of the past, by combining parts of the various processes.

It is not to be inferred from this article that recommendations are made for the encouragement of any particular process, the motive is merely to outline present conditions or, broadly, to show cause and effect, and also to show, if possible, that many elements are as necessary in this industry as in any other, to attain success. Statements have been made to the effect that failures in most instances were due to lack of real engineering skill, and this is partly true, but lack of skill is not wholly accountable for even the engineering failures, for no amount of theoretical engineering skill can replace the knowledge acquired from continued intimate contact with the going operation.

Neither does this statement take into consideration the marketing organization, which is also an essential, and is always confronted with the general economic situation, which does not affect directly the operation.

It can be seen from this outline of the industry that its very existence was primarily due to an unnatural market condition and as the field for profit and exploitation was so enormous it can hardly be wondered at that unusual activity was had in its promotion.

THE EQUIPMENT OF A MODERN SULPHITE PLANT.*

In a paper contributed to the *Papier Zeitung*, Anton D. J. Kuhn contrasts the installation and equipment of a modern Ritter-Kellner cooking plant, with those of a similar outfit, such as was built 15 years ago and was then considered the best arranged plant. He endeavors to point out the changes which the digester and its equipment have undergone and demonstrate the advantages of the modern improvements.

The digester in the old plants was, he says, just the opposite in form to those in modern mills. Where formerly digesters were built of not more than ten to fifteen tons' capacity, they are to be found in operation today of thirty tons' capacity and a short time ago one was planned that would hold thirty-three tons.

The old style digester, spherical or flat at the bottom (see Fig. 1) underwent a change and was replaced by the generally pointed bottom (up to 60°) of the present, while the upper part assumed a hemispherical shape. Owing to the changed form of the digester and by reason of experiments instituted, the perforated plates attached to the digester bottom formerly used have been abandoned. In place of these, to effect the better distribution of the steam and for draining, perforated pipe coils are installed.

The admission of boiling lye and wash water—effected by a different arrangement of the fittings—takes place from below, a proceeding which, as compared with the former style of inlet from above, has many advantages.

The dimensions of the various supports and equipment have been greatly enlarged and loss of time in filling, lixiviating, running off and emptying the digester has been greatly diminished.

Considerable difficulty was experienced with the placing of these great digesters. The old method of construction of placing against the boiler plate a sheet of lead, over which two courses of strong masonry were laid, the joints being closed with litharge and glycerin, is not followed in most new plants. As a rule, in the setting of large digesters, good results have been obtained with a foundation laid on the boiler plate of 2 to 2½ inches in thickness, these being built in over this masonry of bricks. For the foundation as well as for the joints, a mortar consisting of cement, waterglass and ground chamotte (a mixture of broken china and flint) is used. The masonry at the lower and upper neck, which is particularly exposed to wear, is replaced by solidly built-in bronze rings.

The solid building up of the steam inlet and discharge vents had to be changed, as the vibration caused by the rapid boiling, as well as by the quick discharge and washing out, gave rise to excessive shocks to the different outlets. These had consequently

*From Paper.

to be replaced by large boxes, firmly built in, which provided room for play between the inlet and discharge pipe and prevented vibrations from being transmitted to the masonry. A great saving in heat is effected, not only by the employment of previously heated lye, but principally by hot washing of the digester as well as its heavy exterior covering. Even greater economy in steam is obtained where the blowing off of the digester has replaced the older operation. As the cook is not drawn off, the cellulose in the digester is not washed, and the discharge of the cook being accomplished without spray water, the temperature of the digester masonry remains almost unchanged.

Moreover, the first boiling with exhaust steam, so extensively adopted of late years, contributes to further cheapen the cooking. Where formerly in boiling with not highly superheated boiler steam, three quarters to a ton of coal was used per ton of pulp, we manage nowadays with about half this consumption of coal. It must be provided, of course, that the digester be well insulated against loss of heat, that previously heated lye and washing water are used, that the cooking be done with exhaust steam and that the blow off proceeds rapidly.

By means of increased expedition in the cook and a more efficient cooking process, we now obtain an output of 95 to 110 kilogrammes of dry pulp to the cubic meter of digester capacity, per day. Older plants could attain at most 65 to 75 kilogrammes of pulp. Whereas formerly, for a daily output of 10,000 kilogrammes of dry pulp, a digester capacity of $10,000 \div 65 = 154$ cu. meters was necessary, today, by reason of the higher efficiency, with such a digester we can produce in a day $154 \times 100 = 15,400$ kilogrammes of dry pulp, which must be regarded as a remarkably good showing, all things considered.

Still greater is the economy of steam and the cubic-meter efficiency in digesters equipped for blowing out. By the elimination of the discharge and washing time and by the more rapid boiling up and more expeditious emptying, the total dead time is so far reduced, that, keeping up a normal cooking time, an output of 140 to 150 kilogrammes of pulp to cubic-meter digester capacity, per day, has been attained. With this, a digester of 54 cubic meters capacity would turn out daily 154,145 kilos, or the equivalent of 22,330 kilos of dry pulp.

Silos for the storage of the wood chips, such as are now almost invariably disposed above the digester, were formerly seldom seen. The supply for a cooking was then stored alongside of or above the digesters on a flat floor, or in a chip supply wagon made to run on the digester-neck floor (see Fig. 1). This, when the digester was to be charged, had to be run over the digester-neck. The charging, with this and similar arrangements occupied much time and as only a sufficient supply of chips for one cooking could usually be kept ready, nothing must occur in the wood prepa-

ration or transportation departments, if interruption in the cooking was to be avoided.

This is obviated in new plants, by providing a supply of chips sufficient for several cookings, in the silo.

These silos have conical bottoms, lined with smooth sheet iron on which the chips slide well and the filling of the cooker proceeds rapidly.

The chip supply arrangements have been greatly improved of late years and mill architects have contributed to their perfection. Whereas the material was for-

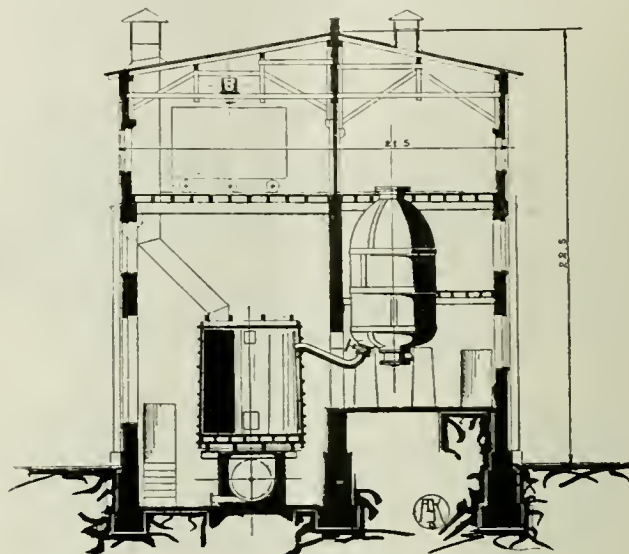


Fig. 1—Sulphite Plant of Older Type.

merly conveyed by means of spiral or scraper conveyors, endless belts, sliding troughs or pneumatic devices are now in use.

THE STUFF VATS.

The digester contents were formerly discharged directly into vats, disposed beneath or at the side of the digester. The lixiviated and washed pulp was then washed by water, through a hose line, from the digester into the vat.

The floor of the vat, laid with boards full of small holes or with perforated filter plates, provided for the thorough drainage of water from the pulp. The pulp could not, however, be drawn completely from the digester into the hose line, and the somewhat burned or browned stuff, adhering to the coils, is let down, through the lower lid, into a special tub or pit, to be worked into 1a cellulose.

The washed pulp is thrown from the tub, or out of the pulp vat, by means of pulp forks, into a stirring apparatus located at the side or beneath it, and is in this diluted and vigorously agitated with clean water. A stuff pump draws off the pulp mass and sends it to the concentrating drum of the finishing apparatus.

Others again threw the stuff from the tubs or pulp vats on to a conveyor belt or into a bucket elevator and forwarded it undiluted for preparation.

New mills certainly resort to these and to similar arrangements, but they have been so much improved that much simpler and more expeditious work is possible. Where for instance one-and-a-half to two hours was required for washing out a 10-ton digester charge, this can now be accomplished, with the aid of the improved and enlarged arrangements, in half an hour. New establishments in which the most complete wood preparing equipments can be installed may without fear of any deterioration of the pulp employ the blowing out process.

In the blow off process the digester charge, with what is left of the gas pressure, is blown out through a strong high blowout duct of large dimensions, extending from the cooker into the vat, partly filled with warm water. A cooker of 10-ton capacity can be emptied, by this means, inside of ten minutes. Through the large, very finely perforated vat filter bottom, the waste liquor, copiously diluted by the warm water and the drainage water from the ventilating pipe, drains off quickly. Repeated thorough washing and vigorous blowing out of the pulp free it from all fine impurities and from acid in the best manner.

If the blowing out vat is placed sufficiently high (see Fig. 2), the pulp may be again diluted and discharged after washing, through large gates in the blowout vat into troughs arranged by the side of it. These are constructed as sand traps and conduct the pulp from finely slit knot drums set up at the end of the trough. From

of the digester, a higher degree of efficiency is insured.

THE COOKER AND VAT BUILDING.

The digester building was formerly constructed almost entirely of brick masonry. The separate stories, as shown in Fig. 1, were formed with iron beams, on which stringers were laid and double flooring. The roof-tree consisted in great part of wood, and buildings thus constructed were much exposed to risk of fire. Fire-walls, iron doors, wire glass windows and other devices may retard a fire, but only in rare cases can prevent the spread of a conflagration.

With the increase in the size of digester, silos and vats, other dimensions and forms had to be given to the building which could not possibly be carried out with the brick masonry. The difficulty was encountered on the one hand in the large sections that brick columns and walls must have for the great height and heavy loading of the building and which required extra space; on the other hand, the building expenses, in the case of brick buildings, were much too high, so that the cheaper skeleton system of construction was preferred (frame of iron or re-enforced concrete with party and exterior walls of masonry).

The digester building shown in Fig. 2 is planned for a 32-ton cooker and blowout vat of corresponding capacity and is designed wholly in re-enforced concrete. The interior of the blowout vat of re-enforced concrete, after floor, walls and cover have been finished water-tight, are durably coated with a kind of stone, prepared especially for this purpose.

The arrangement of the running and tending stages is so planned that the ready observation of all important fittings and apparatus is possible.

The building costs, calculated according to the digester installed, are much lower than formerly. For the erection, for instance, of a 10-ton digester with accompanying vat, an enclosed space of 3,500 cubic meters was formerly required, whereas today, for a 30-ton cooker, only a 4,000 to 4,700-cubic meter enclosed space is required.

The proper calculation of all parts subject to heavy strain and the employment of the best material, obviated the frequent disturbances that occur in the old plants and make consequent repairs unnecessary, thus reducing the cost of maintenance.

Larger digesters and vats than those depicted in Fig. 2 are hardly likely to come into existence during the next few years.

The employment of such large digesters arranged for blowing out is to be recommended wherever the object is to turn out large quantities of pulp of uniform character at a single cooking, as cheaply as possible.

The Tata Hydroelectric Power Co., Ltd., which has about completed a 60,000 h.p. plant in the Bombay Presidency in India, will supply power to 31 cotton mills and 3 flour mills in Bombay, these factories taking from 200 to 2,000 h.p. each.

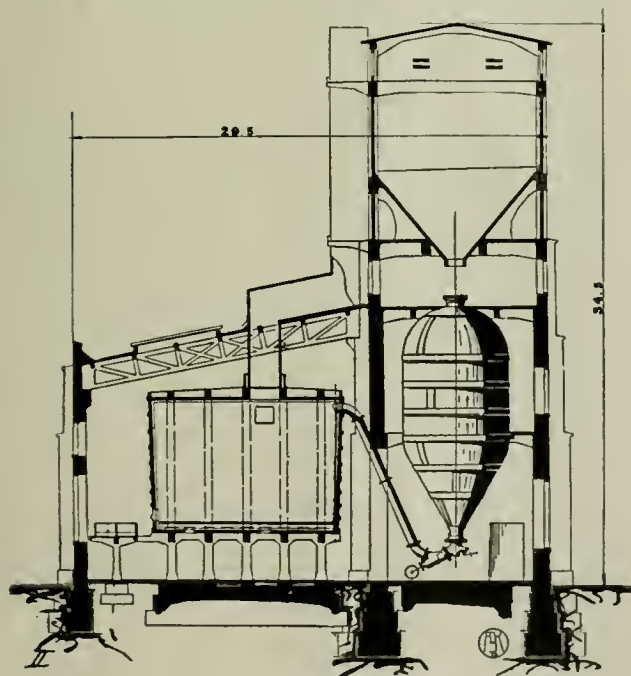


Fig. 2—Modern Sulphite Plant.

the drums, the good pulp is pumped up for finishing. The few that in Germany use the blowing out and washing processes as above described, endeavor to use the digester (as is the case in straw pulp mills) only for cooking, accomplishing the leaching out and washing of the pulp mass in a vat, so that with absolutely uniform pulp quality, by shortening the working period

A YEAR'S OPERATION OF A GAS PRODUCER PLANT.*

Some interesting figures on the cost of operating a gas producer plant at the 27th St. works in Milwaukee, Wis., of the A. O. Smith Co., manufacturer of automobile parts and steel stampings, have been obtained from F. J. Rode, chief engineer of the company. The figures are here presented in tabulated form and show that for the year the cost of operation was 0.634 cent per kw.-hr., and, including the fixed charges, not over 1.104 cent per kw.-hr., with a power factor of 0.71.

The plant includes two 400-kw. units driven by 24x36-in. gas engines built by the Allis-Chalmers Com-

The Smith static tar extractors, already described in these columns, were installed, and, according to Mr. Rode, was the second equipment of its kind. It was found reliable and simple, and that any degree of cleanliness of the gas could be obtained. On tests the gas cleaned with the apparatus contained only one hundredth of the amount of tar as compared with the best results that have been obtained from the old type of rotary washers.

The tar is burned under steam boilers which are used for drop forging and heating purposes, and no credit was allowed to the gas plant, although Mr. Rode explains that 9½ lb. of water were evaporated per pound of tar burned at the boilers. The accumulation

ONE YEAR'S OPERATION OF A GAS PRODUCER POWER PLANT AT FACTORY OF A. O. SMITH CO., MILWAUKEE, WIS.

Month—	Hours of plant running.	Tons of coal consumed.	Cost of coal consumed.	Cost of attendance.	Cost of supplies.	Output, kw.-hr.	Cost of operation per kw.-hr., cent.	Cost of fixed charges per kw.-hr.	Total cost, cent per kw.-hr.	Cost of operating, including fixed charges.	Load factor during time of operation.
January	568	267.7	\$930.00	\$767.75	\$109.75	325,400	0.556	0.279	0.835	\$2,707.50	0.715
February	500	241	903.75	810.40	96.22	284,230	.636	.321	.957	2,710.37	.71
March	554	272	980.00	601.60	87.10	296,620	.565	.301	.866	2,569.05	.665
April	301	168.4	586.00	407.65	63.80	190,700	.556	.464	1.020	1,957.45	.78
May	470	220	792.00	571.95	43.40	236,700	.612	.382	.994	2,318.87	.71
June	244	140	504.00	437.45	48.64	142,000	.697	.633	1.33	1,890.09	.73
July	235	185	660.00	405.45	43.10	134,000	.825	.660	1.485	2,008.55	.715
August	205	110	396.00	396.25	26.10	98,200	.836	.916	1.752	1,718.35	.60
September	230	125	450.00	405.45	34.00	133,000	.670	.677	1.347	1,789.00	.712
October	240	173.5	605.00	422.50	35.20	152,810	.700	.590	1.30	1,960.60	.79
November	215	163.5	590.00	396.55	32.30	144,990	.705	.620	1.325	1,918.85	.837
December	235	178	624.00	383.65	24.60	159,120	.680	.590	1.270	1,932.25	.815
Total	4,000	2,244.1	\$8,020.75	\$6,006.55	\$644.51	2,297,770				\$25,472.00	
Average per mo.	333.33	187	669.33	500.54	53.73	191,480	0.634	0.470	1.104	2,122.00	0.71
Cost of operating, 1913, \$11,672; cost of depreciation, taxes, interest and insurance, \$10,800, or \$900 per month; total, \$25,472.											

pany, Milwaukee. One of these was installed in 1910 and started that year, and in 1911, when the load had increased, the second unit was installed. The gas producer plant includes two producers made by R. D. Wood & Co., Philadelphia, each of 400 hp. rating, and two producers made by the Smith Gas Power Company, Lexington, Ohio, rated at 350 hp. Up to 1912 the plant was operated on hard coal of both buckwheat and pea sizes, but as hard coal prices had gone from \$4 to \$6 per ton, it was decided to operate the plant on soft coal. First Illinois coal was considered, as this could be delivered at \$2.90 per ton at the plant. After experimental operation on different kinds of coal, including West Virginia Splint, Indiana, Illinois and Hocking Valley coals, Hocking Valley nut coal was found to deliver the largest number of kilowatt hours for one dollar. The heat value of the gas averaged 160 B. t. u. per cubic foot, and Sunday Creek Hocking coal showed results as low as 1.5 lb. per kw.-hr., although the average in 1913 was near 2 lb. per kw.-hr.

A saving on cost of operation of 0.3 cent per kw.-hr. was effected by changing to soft coal. The price of the coal varied in 1913, but at the present time the coal is delivered to the gas producers at \$3.50 per ton. The changing from hard coal to the soft coal required a

few modifications in the Smith producer equipment. of tar varies somewhat with the volatile matter in the fuel. The Hocking Valley coal now being used runs from 80 to 100 lb. per ton in the Smith producers. Waste water is used for scrubbing and no charge is made in the record for the water. The waste heat of the gas engine exhaust is utilized, the boiler plant being supplied with the jacket water, which is pumped through gas engine exhaust heaters, and all the excess water is sprayed and cooled for reuse. Repair costs are included in the items of the cost of operating attendance and the cost of supplies. Mr. Rode feels that the only drawback to an otherwise eminently satisfactory equipment is the load factor, which varied to such an extent that probably better results could have been obtained had it remained nearer 0.80 instead of the 0.71 average.

A U. S. Consul reports that American manufacturers might find the Himalaya Mountains, especially Kashmir, where water power is already developed, a good field for the establishment of a lime-nitrogen fertilizer industry, since there are large deposits of lime and the fertilizer could be used for the great agricultural districts in the plains of the Punjab and the United Provinces.

*From the Iron Age.

BY-PRODUCTS FROM NON-COKING COALS*

There are many colliery companies in England the proprietors of which would erect by-product coke ovens if their coals were suitable. Much money has been spent on experimental work, but it has not been found practicable to manufacture metallurgical coke from coal which, under normal conditions, is non-coking, although they are frequently much richer in by-products than many coking coals, so it is particularly unfortunately they cannot be utilized in by-product ovens. However, it is not outside the bounds of possibility to use non-coking coals in processes in which the by-products are recovered. At present two principal alternatives present themselves: (1) Processes of low temperature carbonization, producing smokeless fuel; and (2), the adoption of a producer gas plant working in conjunction with a recovery system. A combination of these two is almost ideal, and the proposition outlined below should be worth the attention of coal owners.

Any process involving the decomposition of coal also involves the production of gas, either in the form of rich gas of 400 to 600 B. T. U., or of producer gas, of a calorific value of 130 to 160 B. T. U. In most cases some use must be made of this gas, for only in exceptional cases can the makers afford to waste it. In a scheme proposed in South Africa, where a large producer plant is to be erected, the coal is so cheap and so rich in nitrogen that it is a paying proposition to work the coal for the sulphate of ammonia.

In general, collieries require quite an appreciable amount of power, and all requirements in this respect could easily be met. Gas-fired boilers, large gas engines and gas turbines, have reached a high state of efficiency, and it might be possible in some cases to dispose of surplus gas to electrical companies, as in the case of the Old Silkstone Colliery Co., of Barnsley, selling coke oven gas to the Yorkshire Electric Power Company for boiler firing.

As suggested, the ideal combination is of low temperature carbonization with gas producers working under recovery conditions. Plants for low temperature carbonization have been before the public very much of late, and although very extravagant claims have been made on their behalf, some of the processes are now sufficiently well-developed to warrant their adoption on a commercial scale. Several plants are under erection at the present time, and very stringent guarantees have been given by the builders. For the gas producer portion several well tried processes of such nature are on the market, successful beyond question.

It might be interesting to consider what could be done with such a plant handling, say, 1,000 tons of coal per week. Next to a coking coal, the best coal for the purpose is one not absolutely non-coking, but that has sufficient of the coking property to form a soft coke. It should be fairly free from sulphur and should con-

tain not more than 8 to 10 per cent of ash. The type of retort heated by a portion of the gas evolved from the coal is perhaps the most suitable for the purpose. The gas would first be denuded of its tar and ammonia, and then washed in creosote oil to extract the benzol, and, if necessary, compressed to extract the whole of the light oils. The yields which might reasonably be expected from a typical Midland coal are as follows:

Coke.	65-70 per cent
Tar.	6-8 per cent
Benzol and light oils.	2-4 gallons per ton
Sulphate of ammonia.	15-25 pounds per ton
Surplus gas.	1,000-2,000 cubic feet per ton

The coke produced would be the smokeless fuel so frequently heard of nowadays. It would not, however, be much of an asset to colliery companies, as a market for it would have to be cultivated. It is very doubtful, too, if the fancy prices expected in some quarters would be realized.

The coke would, in the present proposal, be utilized in gas producers. On an average, it should yield from 60 to 90 lbs. of sulphate of ammonia per ton, and some tar; 650 to 700 tons of the coke would be available per week for gasification in producers; and, taking an average yield of 70 lbs. of sulphate of ammonia, there would be 45,500 to 49,000 lbs., or, say, 20 tons per week. It is hardly advisable to put down a producer plant with by-product recovery with a capacity of less than 500 tons per week; and, of course, the cost per ton gasified, both capital and maintenance, would decrease as the capacity of the plant was increased.

Roughly, 100,000 cu. ft. of producer gas is obtained from a ton of fuel under recovery conditions, so that the weekly yield would be approximately, 65,000,000 cu. ft., of a calorific value of about 140 B. T. U. In producer gas practice none of this gas is actually necessary for working the plant, but steam is required, and the gas can be employed for boiler firing, and all the steam required obtained without extra fuel cost. It is advantageous to operate some portions of the machinery by electricity. For this purpose producer gas is best utilized in gas engines, and if there is any possibility of the sale of surplus power, large gas engine plants could be put down.

The scheme outline is well within the bounds of possibility. There are already large producer plants in successful operation, and the tendency of colliery owners is in the direction suggested. There is a rapidly increasing demand for all the products obtainable from coal, and the prices realized leave a substantial margin of profit. Moreover, the market for all these products seems more than likely to go on increasing; and it is not reasonable to expect that their supply can continue to be limited by the demand for metallurgical coke.

The Japanese in Chosen recently have been using starfish as fertilizing material; it is reported to be excellent for rice. An analysis shows it to contain 4.858 per cent nitrogen and 0.889 per cent phosphoric acid.

*From the Gas World, London, England.



METHODS OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR INSTITUTE OF TECHNOLOGY.

Laboratory Standard Solutions. I.

The laboratory for the general practice of analytical chemistry should be provided at all times with a set of standard solutions for volumetric determinations, and this set should include solutions adapted to all the ordinary volumetric methods.

The methods here outlined have been selected, through experience, as being both accurate and convenient, and are presented in this collected form in the hope that they may be useful to the analyst and possibly to the student of analytical chemistry. To this end the chemical principles upon which the calculations are based are given a little more emphasis than is usually accorded them in descriptions of analytical processes.

All volumetric apparatus in a laboratory should be calibrated at the same temperature. Assuming that this is the case, the volume standard here used is the contents of the measured liter flask at the average laboratory temperature of about 20 deg. C. The variation of laboratory temperature from this is not large in any space of time through which an analytical process will extend. When there are considerable differences in temperature, as between winter and summer, the volume change in the solutions will sometimes be significant, but not usually. In a tenth normal solution, the temperature correction on 50 c.c. of solution for the difference between 20 deg. C. and 30 deg. C. is 0.1 c.c., which is deducted. As the corrections for smaller volumes, and also for smaller temperature variations, are proportional to this, they will ordinarily be smaller than the required accuracy of the determination, if not actually less than the limit of accuracy of the method. It is assumed that the various pieces of volumetric apparatus such as flasks, burettes and pipettes are correctly calibrated with respect to each other.

SOLUTIONS FOR ACIDIMETRY AND ALKALIMETRY.

Standard solutions of acid and of alkali of half normal and tenth normal strength are necessary in every laboratory. Quarter normal solutions are very convenient for nitrogen determinations by the Kjeldahl method upon most materials. A solution of alkali of decinormal strength, and free from carbonates is also essential. Where a considerable number of phosphorus determinations in iron, steel or iron ore are made it is very convenient to have a solution of alkali that is equivalent to 0.005 per cent of phosphorus per

c.c. on a 5 gm. or 2.5 sample, and a solution of nitric acid exactly equivalent to it. Where much food work is done, solutions of acid and alkali for nitrogen determinations are frequently made up in a similar manner.

Indicators.—The choice of indicator to be used in acid-alkali titrations is of the greatest importance, as will be seen through a study of some chemical reactions to be given later. Practically any titration of this character may be made with one of three indicators: i. e., methyl orange, phenolphthalein, or lacmoid.

Methyl orange, as usually used, is the sodium or ammonium salt of a complex organic acid (dimethyl-amido-azo-benzo-sulphonic acid). Sometimes the free acid is used. The indicator solution is prepared by dissolving 0.05 gm. of the pure compound in 200 c.c. of water and filtering. About 4 to 5 drops of this solution is used in each titration. Methyl orange shows a cherry red color in acid solutions if strong and a straw color in bases. The "end point" should always be taken as the first definite *change* in color, and should be an orange color. This indicator may be used to good advantage in titrations which involve the strong acids and the strong or weak bases. It cannot be used for weak acids. HCl, H₂SO₄, HNO₃ are completely neutralized by alkali when methyl orange is used. H₃PO₄ goes to NaH₂PO₄ when NaOH is used. H₂SO₃ goes to NaHSO₃. H₂CO₃, H₂S and chromic acid are neutral to methyl orange, as are the organic acids in general. The color change being not very decided, the "end point" with this indicator requires some practice on the part of the operator, but when once learned, it is very satisfactory. Methyl orange should be avoided, however, if titrations must be made by artificial light, unless the light be very white.

Phenolphthalein is a highly complex and very weak organic acid. It is colorless, but is turned a splendid cherry red by bases. It is very sensitive, and is the best indicator to use for titrations involving weak acids (organic or inorganic) and strong bases. It cannot be used for ammonia or similar bases. Since it may be employed in titrating the weak acids, it must not be used for the titration of any strong acid or base where carbonic, hydrosulphuric or chromic acids may be liberated.

Phenolphthalein indicator solution is prepared by dissolving 1 gm. of the pure substance in 100 c.c. of alcohol. Of this solution, 2 or 3 drops is used.

Lacmoid is a complex dye, whose chemical nature has not been completely worked out. It forms a fine

blue solution, which is turned red by acids. The "end point" is the change from red or blue to violet, and is very satisfactory. It may be used wherever methyl orange is permissible, and is preferred by many to the latter on account of the greater contrast between the acid and the alkaline colors.

PREPARATION OF HALF NORMAL SOLUTIONS OF ACID AND ALKALI FOR GENERAL USE.*

Sodium hydroxide and hydrochloric acid are used.

$N/2HCl = \text{gm. mol. wt.}/2 = 36.45/2 = 18.225 \text{ gm. per liter.}$

$N/2NaOH = \text{gm. mol. wt.}/2 = 40./2 = 20 \text{ gm. per liter.}$

Solution of approximately these strengths are made up as follows:

Acid: Concentrated HCl (c.p.) has a sp. gr. of 1.20 and contains a little less than 40 per cent HCl. This is equivalent to about $1.2 \times 40 = 0.48 \text{ gm. per c.c.}$ 18.225 gm. of HCl would therefore require $18.225/0.48 = 38 \text{ c.c.}$ (about) of strong acid per liter. Since the solution is to be standardized and then diluted to exact strength, it should be made stronger than $N/10$, and some allowance should also be made for the probability that the concentrated acid is not quite up to full strength. To this end, about 10 per cent excess is taken, or 42 c.c. Also, about 200 c.c. more than the amount of solution desired should be made up to allow for the amount used in standardizing. This will require 8.4 c.c. more of the strong acid.

50.5 c.c. of conc. HCl is therefore made up to 1,200 c.c. and the whole thoroughly mixed until homogeneous.

For each additional liter, 42 c.c. of concentrated acid is used.

Alkali: 1,200 c.c. of $N/10NaOH$ requires 24 gms. of the pure body. About 27 gms. of the pure compound is weighed out rapidly, placed on a watch-glass and rinsed off with a little cold water to remove the carbonate from the surface, and then dissolved, and the solution diluted to 1,200 c.c., and the whole mixed thoroughly.

The two solutions, when they attain room temperature, and are perfectly homogeneous, are ready for standardization. Two methods are given.

First Method. This involves the preparation of an exactly half normal solution of sodium carbonate, and the titration of portions of it with the hydrochloric acid solution.

It is very difficult to obtain Na_2CO_3 in a very pure condition. $NaHCO_3$ is, however, obtainable in a state of high purity. Therefore the normal carbonate should be prepared from the acid carbonate. This is done as follows: About 25 gms. of the bicarbonate is placed in a platinum dish and the dish embedded in the sand of a sand bath. A thermometer is placed

with its bulb in the sand beside the dish, and the sand bath heated up to 280 to 300 deg. C., and the whole held at that temperature for an hour. This converts the bicarbonate into the normal carbonate. To be sure of the complete conversion to normal carbonate, it is well to weigh the dish and contents and reheat to constant weight. Of the carbonate thus obtained, 13.2500 gm. is weighed out, dissolved in water, the solution transferred to a measured flask, and made up to exactly 500 c.c. This, after thorough mixing, gives an exactly half normal solution, because, the Na_2CO_3 molecule being equivalent to 2 hydrogen atoms, the gram molecular weight divided by two, and contained in a liter of solution, will give a normal solution. ($M Na_2CO_3 = 106/2 \text{ gms. per liter.}$)

Against measured portions of this solution, from a burette, (about 40 c.c.) the hydrochloric acid solution is standardized by titration, methyl orange or lacmoid being used as indicator. From the relationship of the two solutions, the volume of water per liter which must be added in order to make the HCl exactly half normal, is calculated, this amount of water added from a burette, and the titration repeated. If necessary, dilution and titration must be repeated until the acid solution is exactly equivalent to the carbonate solution, volume for volume.

An entirely similar process is carried out between the standardized acid and the sodium hydroxide solution.

As an example of the calculations used, assume the following data:

40 c.c. of $N/2 Na_2CO_3$ uses 37.4 c.c. HCl solution.

40 c.c. of $N/2 HCl$ uses 39.1 c.c. NaOH solution.

Each 37.4 c.c. of the acid must be diluted to 40 c.c. by the addition of 2.6 c.c. of water. One c.c. then needs $2.6/37.4 \text{ c.c. of water, and } 1,000 \text{ c.c. require } 1,000 \times 2.6/37.4 = 69.5 \text{ c.c. to be added to each liter of solution.}$

Similarly, with the NaOH, $40.0 - 39.1 = 0.9$, $0.9/39.1 \times 1,000 = 23.0 \text{ c.c. to be added to each liter of solution.}$

From these half normal solutions, quarter and tenth normal solutions may be obtained by dilution, in the one case to exactly double volume and in the other, to five times volume.

It is essential for accurate work to check the standard of the diluted solutions by the second method of standardization about to be described.

Second Method. This consists in the precipitation of the chlorine radical of a measured volume of the hydrochloric acid solution by means of silver nitrate, weighing the silver chloride formed, and calculating the standard. 25 c.c. of the HCl solution is taken. To this, after dilution to about four times its bulk, is added a few drops of nitric acid, and a calculated excess of silver nitrate solution. The whole is then boiled until the supernatant liquid is clear, and the silver chloride filtered out upon a Gooch filter previously prepared, dried and at about 150 deg. C., cooled and weighed. The precipitate, after being washed free

*Directions are all based upon the making of one liter of each solution. Much more than this will usually be desired, in which case multiples of the quantities are used.

from silver salts, is dried to constant weight, and from the weight of AgCl , the weight of HCl per c.c. is calculated. From the standard of the solution, the volume of water to be added to a liter of it to make it exactly the required normality is calculated.

An estimation of the quantity of actual chlorine acid present must follow each dilution for accurate work.

$\text{Wt. AgCl} \times 0. = \text{wt. HCl in 25 c.c. of solution.}$ This weight, divided by the weight of HCl in 1 c.c. of $\text{N}/2$ solution (0.01823 gm.) = the number of c.c. of $\text{N}/2$ HCl equivalent to the volume of solution used. From this point, the calculation is finished as indicated in the previous method.

Frequently it is not deemed worth while to make solutions exactly normal, or an exact fraction of normal. In this case, the normality of the solution should be expressed as a factor which when multiplied by the volume of solution used in a determination, will give the number of c.c. of normal, or fractional normal solution equivalent to that volume. This factor is equal to the weight of active constituent per liter, as determined by standardization, divided by the weight of it in a liter of normal or fractional normal. Thus, if a solution of HCl contains, by standardization by weighing AgCl , 18.985 gm. per liter, its normality is 18.985

$$\frac{18.985}{1000} = 1.041 \times \text{N}/2.$$

When standardizing with $\text{N}/2 \text{ Na}_2\text{CO}_3$, as in the first method, the normality is calculated thus:

Assume that 40 c.c. of $\text{N}/2 \text{ Na}_2\text{CO}_3$ uses 38.15 c.c. of the HCl solution. Then the normality of the HCl is $40/38.15 = 1.048 \times \text{N}/2$.

If the acid and alkali solutions are used at all frequently, it certainly pays to make them exactly equivalent the one to the other, c.c. for c.c.. When back-titration of an excess of the one by the other is made, the volume of the second may be directly subtracted from that of the first, when the solutions are equivalent, and the same normality factor employed for both.

In titrating acid and alkali solutions of about tenth normal strength, lacmoid is recommended instead of methyl orange. The end point with the latter indicator is not so sharp with solutions of this concentration, as with stronger solutions, especially in the presence of carbonates.

A number of determinations demand an alkaline solution free from carbonate, notably those wherein weak acids are to be titrated, using phenolphthalein indicator. Owing to the difficulty of freeing even the best caustic soda from carbonate, and the troublesome process involved in preparing a carbonate-free solution from metallic sodium, barium hydroxide solution is recommended for such determinations. A standard solution of it of approximately tenth normal strength is prepared as follows: About twenty grams of barium hydroxide crystals is used per liter of water. Theoretically, 15.775 gm. should be used* because the

crystals of hydroxide always contain a considerable quantity of carbonate. The crystals are dissolved as far as possible in water, and the solution allowed to stand until the precipitate of BaCO_3 has settled completely, the bottle being tightly stoppered. This will take several days as a rule. The clear solution is then siphoned into a bottle in which the air has been replaced by carbon dioxide-free air (pass a current of air through KOH solution and then into the bottle). The bottle is fitted with a two-holed rubber stopper, one hole carrying a syphon, and the other a guard-tube containing soda-lime to keep out the CO_2 of the air. This solution should be perfectly clear, and will remain so a long time if air is kept out. So long as there is no precipitate of BaCO_3 , the standard remains constant, and of course the solution is free from CO_2 . The solution is standardized against the laboratory's standard hydrochloric acid, and its normality calculated. It is not wise to try to dilute it to exactly tenth normal, on account of the risk of precipitating the carbonate by CO_2 from the air or from the water used in diluting.

(To be continued.)

THE ANALYTICAL CONSTANTS OF HYDROGENATED OILS.*

By CARLETON ELLIS.

The hydrogenation of oils has to such an extent changed certain of the constants by which oils and fats are at least in part identified, namely, the iodine number and the specific gravity, that the identification of a fat or fatty mixtures, often heretofore a troublesome matter at best, now promises to become even more difficult.

The reduction of the iodine number through the introduction of hydrogen into the oil, in a sense is arbitrary; there is no difficulty in reducing the iodine number almost to zero through the hydrogenation process, or at any moment to interrupt the operation and from one and the same initial material to produce products having the most varied iodine numbers.

The specific gravity and melting point advance hand in hand as saturation progresses, the specific gravity approaching that of tristearine, while the resultant melting point in considerable measure depends upon the molecular weight and the hydroxyl content of the fatty acid components of the oil. The specific gravity of a hardened cottonseed oil whose iodine number had been reduced to zero was found by Normann and Hugel¹ to be 0.9999 at 15°C ., while they note that tristearine has a specific gravity of 1.0101 at the same temperature.²

The index of refraction also is strongly modified. A sample of fish oil at 56°C ., according to Normann and Hugel, showed a figure of 53.8; while after hardening to an iodine number of 22.5 the index was 36°C . at the same temperature. (Scale of the Zeiss butter refractometer.)

* $\text{Ba}(\text{OH})_2 = 315.5$, and is equivalent to 2 H, so a normal solution would contain one-half of this weight in grams per liter.

*From The Journal of Industrial and Engineering Chemistry.

Observations made in the writer's laboratory on the index of refraction of a number of hydrogenated oils gave the results noted below:

INDEX OF REFRACTION AT 55° C.
(Abbé Refractometer.)³

	Original Oil.	Hydrogenated Oil.
Corn	1.4615	1.4514 (M. P. 55.7° C.)
Whale (No. 1)	1.4603	1.4550 (M. P. 41.5° C.)
Soya bean	1.4617	1.4538 (M. P. 50.3° C.)
Cocanut oil ("olein")	1.4429	1.4425 (M. P. 24.7° C.)
Linseed	1.4730	1.4610 (M. P. 42.3° C.)
Palm	1.4523	1.4517 (M. P. 38.7° C.)
Palm	1.4523	1.4494 (M. P. 44.8° C.)
Peanut (edible)	1.4567	1.4547 (M. P. 34.7° C.)

The gradual reduction of the index of refraction by progressive hydrogenation is shown in the following table compiled from determinations made in the writer's laboratory.

Cottonseed oil was hydrogenated for a period of ten hours and samples were drawn at one hour intervals.

It is of interest to note that while the addition of *hydrogen* to fatty oils reduces the index of refraction, the addition of *oxygen* increases the index as is shown in the case of blown or ozonized oils.

Original Oil	Melting point.	Index of refraction.
	55° C.	
1 hour	28.2° C.	1.4588
2 hours	31.3	1.4577
3 hours	34.3	1.4568
4 hours	37.9	1.4557
5 hours	40.8	1.4549
6 hours	43.8	1.4540
7 hours	45.6	1.4527
8 hours	47.3	1.4518
10 hours	55.9	1.4510
		1.4496

The saponification number practically does not change. The content of free fatty acids changes but little. A sample of cottonseed oil containing 1.8 per cent fatty acid was found, after hardening to various degrees, to have a fatty acid content ranging from 1.4 per cent to 1.9 per cent. With sesame oil containing 2.44 per cent fatty acid the resulting hardened oil contained 2.55 per cent of acid. The content of unsaponifiable bodies does not essentially change. Cottonseed oil having 0.55 per cent unsaponifiable matter, after hardening, showed a content of unsaponifiable bodies ranging from 0.45 per cent to 0.55 per cent; sesame oil with an unsaponifiable content of 0.70 per cent, after hardening contained 0.85 per cent unsaponifiable.

Cholesterol and phytosterol, according to Bomer, are not changed by treating oils with hydrogen, although this is somewhat contrary to the statement of Windaus,⁴ according to whom cholesterol may be easily reduced by the catalytic process. Willstätter and Mayer⁵ hydrogenated cholesterol in ether solution with a platinum catalyzer.

In the case of the acetyl number more noticeable changes take place according to Normann and Hugel. When hardening castor oil, for example, the hydroxyl

number in one sample dropped from 156 to 102; in another sample the number fell to 131. The hydroxyl group is thus more or less broken down by the hydrogenation process, at least under some conditions of treatment.

Acid number	3.5
Saponification number	183.5
Iodine number	4.8
Acetyl number	153.5
Acetyl number of the fatty acids	143.1
Acid number of the fatty acids	184.5
Saponification number of the fatty acids	187.9
Melting point of the fat	68° C.
Melting point of the fatty acids	70° C.
Melting point of the acetylated acids	47° C.

The properties of hardened castor oil have been noted by Garth,⁶ whose observations differ somewhat from those of Normann and Hugel. As is generally known, castor oil differs materially from many other common oils in such respects as its high viscosity, solubility in alcohol and difficulty of salting out its soaps by electrolytes. Hardened castor oil dissolves in alcohol only by heating and separates on cooling, but is soluble at ordinary temperature in chloroform. The constants of one sample of hardened castor oil examined by Garth are given in the above table.

These results obtained by Garth would indicate that the saponification and acetyl number do not change. The iodine number has fallen greatly and the melting point is much increased. The difference between the acid number of the fatty acids and their saponification number points to the formation of lactones. As is known castor oil has the property at high temperatures of forming anhydrides, accompanied by polymerization.

The effect of hydrogenation on color tests of oils is variable. Thus the Boudouin sesame oil test is not influenced; in fact the reaction seemingly is sharper after treatment of the oil with hydrogen, while the Halphen test is not likely to give positive results even with oils which have been only slightly hardened.

The Becci test is operative with slightly hardened cottonseed oil, but is indistinct with highly hardened oil so that this test is significant only in event of a positive coloration.

Hardened fish oil loses all its essential characteristics such as the formation of well defined bromine compounds of the higher unsaturated fatty acids. Thus there are obtained after hardening, new fatty acids corresponding to the saturated bodies, arachidic ($C_{20}H_{40}O_2$) and behenic acids ($C_{22}H_{44}O_2$), which in variable amounts up to a proportion of 20 per cent and more have been observed in certain hydrogenated oils. In the hardening of rape oil behenic acid is formed from the erucic acid present. Other oils or fats with a noticeable proportion of acids with more than 18 carbon atoms in the molecule apparently scarcely ever come into the trade.

As a test for hydrogenated peanut oil, Krciss and Roth⁷ have given a method which consists in saponi-

¹ Chem. Ztg., 1913, 815.

² The specific gravity of tristearine is given by the "Chemiker Kalender" as 1.0101 at 15° C., while Lewkowitsch reports the specific gravity of a specimen of not quite pure stearine in the melted state as 0.9235 at 65.5° C.

³ Refraction values are given in terms of true refractive index and also according to the arbitrary scale of the butyro-refractometer, in order to follow the data available, as rendered.

⁴ Ber. d. Chem. Ges., 1912, 3051.

⁵ Ibid., 1908, 41, 2199.

⁶ Sellen Ztg., 1912, 1309.

ying 20 grams of the oil with 40 c.c. of alcoholic potash; then adding 60 c.c. of alcohol and acidifying by the addition of 50 per cent acetic acid of which approximately 15 c.c. are required. One and one-half grams of lead acetate are added and the mixture allowed to stand over night. The lead salts which separate are decomposed by boiling with 5 per cent hydrochloric acid, the fatty acids are dissolved in 50 c.c. of 90 per cent alcohol with slight warming and the solution is placed in water at 15° for about one-half hour. The crystals which separate are recrystallized from 25 c.c., then 12½ c.c. of 90 per cent alcohol and the melting point determined. The presence of at least 5 per cent arachidic acid causes the melting point of the third crystallization to be over 70° C.

Normann and Hugel⁸ state that this test is applicable likewise to hardened fish and rape oil. They tested a number of samples of fish oil from several sources and found in each case that the melting point of the recrystallized fatty acids was at least 70°. Normann and Hugel state that it is unnecessary with hardened fish oil to allow the lead acetate to react for several hours, it sufficing simply to let the mixture stand until cooled to room temperature; this can be hastened by cooling with water. So large a proportion of fatty acids is obtained according to this procedure that the specified amount of alcohol is not sufficient to dissolve them. It is better to use 100-150 c.c. of alcohol and heat on the water-bath until solution is affected. The application of heat should not be continued for any great length of time as arachidic acid readily forms esters. The mixture is then placed in cold water, cooled to room temperature and the separated material collected and crystallized several times from alcohol used in progressively diminishing proportions. Three crystallizations suffice for only slightly hardened fats. With fats of higher consistency one must recrystallize several times more until the melting point is constant.

In one case using hardened fish oil having a melting point of 44, three recrystallizations from alcohol gave a constant melting point of only 63°, while further recrystallization using acetone caused the melting point to advance to 76°. In doubtful cases one should try several solvent mediums. If the melting point is found to be above 70° C. Normann and Hugel think it proof that either hardened fish, rape or peanut oil is present. If one is certain of the unitary character of the oil then peanut and rape oil can be distinguished from fish oil by the cholesterol test, provided the statement of Bomer in regard to the unchangeability of cholesterol and phytosterol under ordinary conditions of oil hydrogenation is confirmed.

Data on hardened oils by Davidsohn⁹ are tabulated below:

	M. P.	Acid No.	Sapon- ifica- tion No.	Mois- ture.	Ash.
Talgol	39.3	3.4	191.0	0.10	0.07
Talgol extra	46.5	3.5	191.3	0.13	0.05
Candelite	49.0	3.2	191.0	0.20	0.08
Candelite extra	51.9	3.9	190.8	0.15	0.04
Coryphol	79.3	3.3	189.9	0.18	0.05

These hardened fish oils or other hardened oils put out under the trade names indicated are manufactured by the Germania Oil Works of Emmerich.

Knapp¹⁰ states that the attention of analysts should be directed to the fact that in the immediate future they will be called upon to analyze certain new artificial fats prepared by hydrogenation and, not improbably, to detect their presence as adulterants. Thus, for example, starting with olive oil, as the absorption of hydrogen proceeds, a turbid oil, then a liquid magma, then a soft fat, and finally a hard fat, is obtained. Knapp observes "A similar change occurs with all oils containing glycerides of unsaturated acids. This rise in the melting point is naturally accompanied by a decrease in the iodine value and refractive index. Fats have been prepared in this way from cottonseed oil with iodine values as low as 5, and if desired the iodine value could doubtless be reduced to 0, and the melting point raised to 60°-70° C. While it is too costly for commercial purposes to carry the saturation of the unsaturated glycerides to completion, it might be of value in the laboratory as an aid to determining the component glycerides in a pure oil. Not only the oils containing glycerides of oleic acid can be hardened, but also those containing glycerides of linolic acid and linoleic acid (the drying oils), and even of such highly unsaturated acids as clupanodonic (in whale oils). Any one who has seen a malodorous oil converted into a bland odorless tallow realizes the commercial possibilities of the process. And when it is remembered that the process can be stopped when the iodine value reaches a desired number, the possibility becomes evident of the preparation of a fat with any required analytical figures." In support of the foregoing, Knapp furnishes the following data:

Original oil	Hardened oils		
	Solid particles floating in oil	Soft greasy solid	Brittle solid
Appearance.....	Clear liquid		
Butyro-refractometer (corrected to 40° C.).....	57.7	..	47.7
Fatty acids			
Iodine value....	110	94	55
Titer.....	34.7° C.	37.0° C.	42.5° C.
Neutralization value (mg. KOH)....	197	196	192

The analyst is chiefly interested in the question of how these fats are to be detected. It is doubtful if their most characteristic feature, the relatively high percentage of stearic glycerides which they contain, will be of much service. Knapp states that until the manufacturer accomplishes the difficult step of com-

⁷ Chem. Ztg., 1913, 58 and 369.

⁸ Ibid., 1913, 815.

⁹ *Öl- und Fetthdl.*, 1913, Nos. 14 and 15, and *Seifen Ztg.*, 1913, 529.

¹⁰ The Analyst, 1913, 102.

¹¹ Too much reliance should not be placed on the nickel test as evidencing the presence or absence of hydrogenated oils. It is known to the writer that hardened oils which are free from nickel are on the market, these in some cases presumably having been prepared with the aid of palladium as a catalyzer.

pletely removing the nickel, the detection of traces of this metal will be the simplest and most reliable test for hardened oils.¹¹ Although the catalyst is very finely divided, the manufacturer can obtain a perfectly clear fat by careful filtration, and hence it is the nickel contained in the nickel soaps formed by the free fatty acids present that one has to detect. The following method is suggested: 50 grams of the fat are heated in a flask with 20 c.c. hydrochloric acid, with continued vigorous shaking. The mixture is allowed to separate while hot, and part of the acid solution is evaporated to dryness, dissolved in a drop of water and placed on a white tile. One drop of ammonium sulfide is added to this and also to a drop of water for comparison. Knapp, however, tried this test only on a few hardened oils, and in some cases with negative results. Dimethyl-glyoxime is a much more delicate test, but unfortunately Prall has found¹² that certain pure untreated oils give a red coloration. Hence further investigation is needed.

One of the most characteristic tests for fish oils—the bromide estimation—is quantitatively useless for these oils after hardening, as the percentage of ether-insoluble brominated glycerides is greatly reduced thereby. Not only are the analytical figures for the oils altered by this absorption of hydrogen, but also the traces of substances which often serve as a useful test for the particular oil in which they occur—*e. g.*, Halphen's reaction. Knapp believes Bomer's observation that phytosterol and cholesterol are not changed in this process is of great analytical value.

Three fats obtained by Knapp from a clear cottonseed oil, hardened by hydrogen with the help of different catalysts, gave the following figures:

Catalyst	Percentage of catalyst in oil	Character of product	Butyro-refraction (Corrected to 40° C.)	Melting point °C.
Nickel.....	1.00	Hard	45.7	49
Platinum.....	1.10	Hard	47.8	46
Palladium.....	0.06	Brittle	45.5	52

The keeping properties of these hardened oils were found to be remarkably good. Although prepared nearly a year and a half previously and having often been exposed to damp air, yet they showed no signs of rancidity. The free acidity (0.70 per cent as oleic acid) did not appreciably change during the period of observation.

Bomer¹³ is in substantial agreement with the foregoing, for he states that (1) the hardened oils, as a result of the more or less complete transformation of unsaturated fatty acids (oleic, linoleic, linolenic) into stearic acid, show an increase in the melting and solidifying points as well as a lowering of the refractometer number and iodine number while the saponification number is but little altered.

(2) Judging by the iodine numbers of the liquid fatty acids, these acids appear to be not uniformly transformed into stearic acid, but the transformation of oleic acid appears to progress more slowly than the less saturated linoleic and linolenic acids, etc.

(3) Among the hardened oils, the soft and medium hard products, in color, consistency and in part also in odor and taste, show, a greater or less similarity to beef or mutton tallow, so that by external appearance one cannot distinguish these hardened oils from such animal fats; for example medium hard peanut oil is so completely like neutral lard, and hardened whale oil is so like mutton tallow, that one is not able to distinguish between these fats by appearance, consistency, odor nor taste.

(4) Not only in their outward properties are these hardened oils like hog fat and mutton tallow, but also the usual analytical constants are so similar that one cannot distinguish some samples of hardened peanut oils and hardened sesame oil from hog fat, nor whale oil, in some cases, from mutton or beef tallow. In the latter case even the Polenske numbers agree while in the case of sesame oil they are somewhat lower than hog fat.

Oil	Appearance	Melting point	Solidifying point	Refractometer at 40°	Acid No. (a)	Saponification No.	Iodine No.
Peanut oil untreated	Yellow liquid....	..	..	56.8	1.1	191.1	84.4
Peanut oil hardened	White tallowy ..	51.2	36.5	59.1	1.0	188.7	47.4
Sesame oil hardened	White tallowy ..	62.1	45.3	58.1(b)	4.7	188.9	25.1
Cottonseed oil hardened	Yellowish lard like..	38.5	25.1	53.8	0.6	195.7	69.7
Cocoanut oil untreated	White soft	25.6	20.4	37.4	0.3	255.6	11.8
Cocoanut oil hardened	White lard like..	44.5	27.7	35.9	0.4	254.1	1.0
Whale oil hardened	Yellowish tallowy ..	45.4	33.7	49.1	1.1	193.0	46.8

(a) Milligrams potassium hydroxide for 1 gram fat.

(b) Determined at 50° C.

Bomer examined a number of hydrogenated oils and tabulated the results of his investigations and from these the above condensed table has been compiled.

The solid and liquid fatty acids separated from the hydrogenated fat by the method of Farnsteiner showed the following properties:

Oil	Solid fatty acids		Liquid fatty acids	
	M. P.	Acid No.	Refraction at 40° C.	Iodine No.
Peanut oil untreated	...	...	47.6	91.8
Peanut oil hardened	...	199.7	42.9	82.9
Sesame oil hardened	56.4	199.5	44.7	88.9
Cottonseed oil hardened	45.0	206.8	48.3	115.6
Whale oil hardened	...	199.5	44.4	96.0

Samples of these hardened oils were examined for cholesterol and phytosterol. Hardened peanut oil was found to contain 0.4 per cent, sesame oil 1.0 per cent, cottonseed oil 1.6 per cent, and whale oil 0.2 per cent of sterol, of which the three first hardened products mentioned exhibited the typical crystalline form of phytosterol. The melting point of these sterols ranged from 132 to 139° C., yielding acetates melting between about 126 and 129° C. The hardened whale oil gave a sterol melting at 149.7° C.

Bomer made a series of fractional crystallizations of hardened oil and from a sample of hydrogenated

¹² Bomer, *Zeltsch. Untersuch. Nahr. Genussm.*, 1912, 21, 104; and *Analyst*, 1912, 37, 452.

¹³ *Chem. Rev. u. d. Fett und Harz Ind.*, 1912, 220.

peanut oil obtained tristearine (amounting to about 2-3 per cent). Bomer has called attention to the rather striking behavior of cocoanut oil. He calculated from the iodine number that the natural oil contained 13 per cent of oleic acid and after hydrogenation approximately about 1 per cent of this acid was present. As a result of the transformation of 12 per cent of oleic acid into stearic acid, the melting point increased from 25.6° C. to 44.5° C., or thus 18.9° C., while the solidifying point advanced from 20.4° C. to 27.7° C., or only 7.3° C.

A species of hardened fish or whale oil known as "Talgit" has been examined by Müller,¹⁴ who found the product to have an acid value of 12.8, an iodine number of 40 and a titer (fatty acids) of 39.4° C. The fat was saponified and pressed to obtain stearic acid. It was found that the operation of pressing could be carried out effectively to yield a product technically free from liquid fatty acids: 35 per cent of solid fatty acid having a titer of 48.7° C. was thus obtained. Müller states that since mixtures of stearic and palmitic acids possess a solidifying point above 53.5° C. the low titer of the solid acids of Talgit points to the presence of solid acids other than stearic and palmitic. Dubovitz¹⁵ thinks the low melting point to be due to the presence in the original fish or whale oil of hypogaic and physetoleic acid or similar acids with possibly unsaturated fatty acids of a still lower number of carbon atoms.

Leimdorfer¹⁶ regards the stearine produced by the hydrogenation of some oils to be perhaps an allotropic form of natural stearine.

An attempt is made by Grimme¹⁷ to identify fish oils after they have been hardened. As stated, the ordinary constants give no clue to the original source of a hardened oil and hence Grimme resorts to color reactions. A list of tests is given for each of the four classes of fish oils: (1) Seal oils; (2) Whale oils; (3) Liver oils; (4) Fish oils; and also characteristic tests for individual oils. These tests were also applied to two hardened oils of unknown origin and Grimme believes from his results that the color reactions are characteristic enough to establish the presence of fish oils. Nickel was found in the samples, Fortini's test (as detailed below) giving the strongest coloration. Color reactions were applied to six authentic whale oils from two different sources, and hardened to different degrees. These tests were carried out by dissolving 5 parts of the sample in 95 parts of benzine-xylene (1:1) and agitating 5 c.c. of the solution with the reagent; after 5 minutes and 60 minutes the color was noted. Grimme finds the iodine-sulfuric acid reaction (1 c.c. concentrated sulfuric acid and 1 drop tincture of iodine) to give a characteristic violet-red color for whale oil though the intensity of coloration decreases with increasing hardness. The constants of the six

samples of hydrogenated fish and whale oils employed and the coloration produced by different reagents are tabulated by Grimme.

A draft of the Codex alimentarius Austriacus, which has been prepared by a board of prominent chemists and officials including Hefter, Wolfbauer, Fischer, Hartl and Pellischek,¹⁸ embraces the subject of hydrogenated oils and it is stated that considered as a food product these oils will require further careful investigation before it is determined with certainty just what rank they will take as edible products. It is noted that the fats now offered for edible purposes are white to yellowish in color, almost odorless and tasteless. Usually the consistency lies between that of ordinary butter and hard tallow. Now and then samples are found which melt at about 60° C. and are as brittle as carnauba wax. These hard products, of course, are not intended by themselves to be used for edible purposes, but are employed to raise the melting point of soft fats. Samples of hardened peanut and sesame oil with iodine numbers reduced to 50 or lower, sometimes down to 20, have been examined. Cocoanut oil with an iodine number of 2 or even lower has been met with. The cholesterol of animal fats and the phytosterol of vegetable oils is not altered by the hydrogenation process. The hardened fats, it is stated, scarcely ever appear on the market in their true light but usually are put out under some trade name such as "Peanut-oleo," "Sesame-oleo," "Peanut-margarine," "Sesame-margarine," "Crisco," and the like.

Hardened oils examined by Aufrecht¹⁹ in outward appearances resembled palm kernel oil. They were very hard and of granular fracture, were either pure white or yellowish in color. A distinct odor was perceptible on melting or heating. The taste recalled that of tallowy fats. The products were readily soluble in the usual fat solvent mediums, but the solubility in methyl and ethyl alcohol was very slight. The facts were easily saponifiable. The content of free fatty acid fluctuated between 0.51-0.83 per cent. The ash reacted alkaline and consisted of alkali carbonate and traces of iron oxide, but no nickel or other constituent could be detected. The following analytical results are given:

	1. Durotol (yellow)	2. Durotol (white)	3. Hydrogen- ated Tran.
Color	yellowish	white	white
Specific gravity at 15° C.	0.9252	0.9257	0.9268
Melting point °C.	46.5	46	48
Solidification point °C.	43.5	43.5	45.5
Viscosity at 50° C.	5.4	5.4	5.6
Acid No. (calculated as oleic acid)	0.51	0.57	0.83
Saponification No.	162.2	161	173.5
Unsaponifiable matter (per cent)	1.92	2.1	2.4
Acetyl No.	1.2	1.2	0.95
Iodine No.	3.9	4.2	7.8
Hehner No.	95.8	95.8	96.4
Reichert-Meissl No.	0.38	0.36	0.52
Water	0	0	0
Ash	0.037	0.03	0.05

The detection of traces of nickel by the usual analyt-

¹⁴ Seifen Ztg., 1913, 1376.

¹⁵ Ibid., 1914, 1445.

¹⁶ Ibid., 1913, 1317.

¹⁷ Chem. Rev. u. d. Fett und Harz Ind., 1913, 129 and 155.

¹⁸ Seifen. Ztg., 1913, 1087.

¹⁹ Pharm. Ztg., 1912, 876.

ical methods is often difficult. Dimethylglyoxime, proposed by Tschugaeff, is a reagent of great sensitivity. Its application has been investigated by a number of chemists, and among these Bianchi and DiNola²⁰ report that the presence of copper and iron interferes with the test. They worked with an acid reagent and used the following procedure:

To the substance supposed to contain nickel one or two drops of concentrated hydrochloric or nitric acid are added and the acid solution so obtained is placed in a porcelain dish, or preferably on a strip of filter paper. A few drops of ammonia are added, or in case the strip of filter paper is used, this may simply be exposed to the vapors of ammonia. The liquid is acidified with acetic acid and a drop of concentrated alcoholic solution of dimethylglyoxime is added. The presence of nickel is shown by a red coloration which grows more pronounced in the course of time. This reaction is a very simple one and does not require any particular technical knowledge for carrying out.

Fortini²¹ has simplified this reaction and uses an alkaline instead of an acid reagent which apparently gives more satisfactory results than the above procedure. Fortini mixes one-half gram of dimethylglyoxime, 5 c.c. 98 per cent alcohol, and 5 c.c. concentrated ammonium hydroxide in the order as given, yielding a clear, faintly yellowish liquid which in glass-stoppered bottles may be kept for a long time unchanged. The test is carried out as follows:

The sample to be examined is freed from fat by extraction with ether and to the residue a drop of the reagent is added. When nickel is present there will appear in a few seconds a rose colored flock caused by reaction with the nickel oxide present on the surface of the metallic nickel. Of course, if nickel is present in the form of a soap, the fat should be extracted with, for example, aqueous hydrochloric acid in the manner prescribed by Knapp in the foregoing. In order to make the reaction even more sensitive, the residue may be heated for a few moments in an oxidizing flame to produce nickel oxide.

The detection and determination of small quantities of nickel by α -benzildioxime is described by Attack²² as follows:

An alcoholic solution of α -benzildioxime gives with nickel compounds a bulky red precipitate which is insoluble in water, alcohol, acetone, 10 per cent acetic acid, and ammonia; the precipitate becomes reddish yellow on boiling. The reagent is much more sensitive than dimethylglyoxime, showing 1 part of nickel in 5 million of water, and the precipitate is readily filtered.²³ Small quantities of nickel are determined as follows: 150 c.c. of a hot saturated alcoholic solution of the oxime are added for every 0.01 gram of nickel, the mixture is heated for a few minutes on the water-bath, filtered, the precipitate washed with hot alcohol, and dried at 110°-112° C.; it has the formula $C_{28}H_{22}N_4$,

O_4Ni and contains 10.93 per cent Ni. Nickel may be separated from cobalt in ammoniacal solution. α -Benzildioxime is prepared by boiling 10 grams of benzil, dissolved in 50 c.c. of methyl alcohol, with a concentrated aqueous solution of 8 grams of hydroxylamine hydrochloride, for 6 hours, washing the precipitate with hot water and then with a small quantity of ethyl alcohol, in which it is only slightly soluble. It may be crystallized from acetone.

The hydrogen value is proposed by Fokin²⁴ as a means of determining unsaturated organic compounds in a manner similar to the iodine values of Hubl and Wijs.

The "hydrogen value" of an organic compound is defined as the number of cubic centimeters of hydrogen (at 0° and 760 mm.), which are absorbed by 1 gram of the compound. For the test, an apparatus is devised consisting of a distillation flask (50-150 c.c.) having a small beaker fused inside on the bottom, and connected by means of the side-tube to a gas burette and a gasometer containing hydrogen. In the small beaker are placed about 0.1 gram of catalytic platinum, moistened with 15 c.c. of water, and in the flask the substance to be examined and 20-30 c.c. of alcohol free from dissolved oxygen. Hydrogen is admitted and the flask is shaken by a shaking machine until absorption is complete. The following hydrogen values were obtained by Fokin, the figures in parentheses being either hydrogen values corresponding with Wijs' iodine value, or, where indicated, the theoretical hydrogen values. Elaidic acid, 78.6-81.4 (78.8); oleic acid, 86.2-87.2 (86.2); fatty acids from sunflower oil, 119.6-120.8 (122.9); fatty acids from linseed oil, 164.9-166.3 (166.0); castor oil, 73.7 (75.5); croton oil, 260.9 (theoretical, 258.4); undecic acid, 115.6 (114.1); erucic acid, 39.4 (65.6). Colophony does not absorb hydrogen under the conditions of the test. The "hydrogen value" of course is not a determination as yet of use in the identification of hardened oils, but is noted here because of its incidental interest.

The foregoing embraces most of the information available from published sources on the analytical side of hydrogenated or hardened oils and it is hoped that the very meagreness of the data may serve as a stimulus for abundant investigations tending to clarify the subject and enabling fairly definite procedures to be adopted for the qualitative and quantitative examination of these products.

In 1912 the commercial product of coal in Alaska amounted to only 335 tons. In addition 900 tons were mined under the direction of the Bureau of Mines for testing by the United States Navy. The imports of coal into Alaska amount to about 100,000 tons annually. Most of the transportation and manufacturing industries of the territory, however, depend on oil for fuel.

²⁰ Chem. Ztg., 1913, 37, 773.

²¹ Compare Ibbotson; J. S. C. I., 1911, 1317.

²² J. Russ. Phys. Chem. Soc., 40 (1908), 700, J. Chem. Soc. Abstr. 91 (1908), 11, 637.

²³ Boll. Chim. Farm., 1910, 517.

²⁴ Chem. Ztg., 1912, 1461.

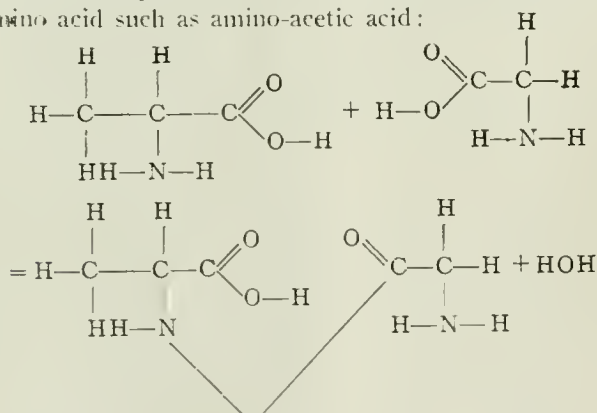
A RAPID METHOD FOR DETERMINING THE PERCENTAGE OF CASEIN IN MILK.*

By W. O. WALKER.

During the past few years dairymen have been giving a good deal of attention to the advisability of taking into account the percentage of casein when paying patrons for milk to be used in cheese-making. Some advocate paying on a fat basis only, others on the fat and casein basis. It is not the object of this article to discuss the merits of either of these methods, but to outline a process which has been tried out in the author's laboratory for quickly and simply arriving at the amount of casein in milk.

It is well known that several methods have been suggested of late, the most promising probably being the centrifugal method of Hart. This has, apparently, yielded satisfactory results in many cases, but has been found to give varying results with preserved samples, and with fresh milk, under different conditions of temperature, etc.

Research into the constitution of the protein molecule has revealed the probability of its consisting of a complex linkage of a large number of amino acids. To illustrate this linking up of amino acids we may use the following equation, which shows how one molecule of a simple amino acid, such as amino-propionic acid, may become bound to a molecule of another amino acid such as amino-acetic acid:



Both the molecules of amino-propionic acid and amino-acetic acid, as indicated above, possess an alkaline (amino) group, $\text{H}-\text{N}-\text{H}$, as well as an acidic

group, $-\text{C}(=\text{O})\text{OH}$, and when they combine we may

have the union taking place in the manner indicated, in which the alkaline (amino) group of one molecule interacts with the acidic group of the other molecule, thus leaving an alkaline group and an acidic group still existing in the product, which may be looked upon, for our purpose, as a very simple representative of the proteins.

It has further been observed that when formaldehyde is added to proteins, the neutral character of the molecule disappears, with the result that the acidic property predominates strongly. It is thought that

the formaldehyde reacts with the alkaline groups forming methylene derivatives, thus leaving the acidic groups free to act. These acidic groups may now be neutralized with standard alkali, and if the value of the alkali in terms of protein be known, the percentage of protein present may be estimated.

Hugo Schiff¹ was the first to point out the importance of the reaction between formaldehyde and amino acids. S. P. L. Sorensen worked out most of the details for the quantitative application of the reaction for estimating amino acids. H. Droop Richmond adapted the reaction to the estimation of total proteins in milk.

The author decided to apply the reaction to the estimation of casein in milk, with the use of the alkali commonly used for the "acid test" now in general use in cheese factories in Ontario.

In hoping to apply the reaction to estimate casein only, the problem is, of course, to obtain the proper factor, which, when multiplied by the quantity of alkali necessary to neutralize the acidity developed after treatment with formaldehyde, will give the quantity of casein in the sample. Since the formaldehyde reacts with both casein and albumin, and, since the amounts of these two in milk do not bear a constant ratio to one another, it was not to be expected that a factor holding good in all cases could be obtained. However, a factor has been obtained that is giving unexpectedly good results.

The alkali solution was ninth normal sodium hydroxide, and the formaldehyde was the commercial article (40 per cent) made neutral to phenolphthalein.

The method for arriving at the factor was the following: 10 c.c. of milk were transferred by means of a pipette to a porcelain casserole. A fairly large quantity of phenolphthalein solution (about 1 c.c. of a 1 per cent solution) was added next. The alkali was then run in with constant stirring with a glass rod until a fairly deep pink color developed. So far the test is exactly the same as the ordinary "acid test." No account was kept of the alkali used to bring the sample of milk to the neutral point. About 2 c.c. of the neutral formaldehyde solution were next added, with the result that the pink color at once disappeared. The reading of the burette was then taken, and alkali again added with stirring until the same degree of color developed. The reading of the burette was again taken, the difference between the two readings being the amount of alkali used in the second titration.

Sample.	Kjeldahl method.	New method	Difference.
1.....	2.45	2.53	+0.08
2.....	2.45	2.45	0.00
3.....	2.61	2.63	+0.02
4.....	2.51	2.52	+0.01
5.....	2.77	2.69	-0.08
6.....	2.53	2.61	+0.08
7.....	2.32	2.36	+0.04
8.....	2.96	2.96	0.00
9.....	2.69	2.66	-0.03
10.....	2.45	2.36	-0.09
11.....	2.32	2.30	-0.02
12.....	2.52	2.56	+0.04
13.....	2.31	2.27	-0.04

*From The Journal of Industrial and Engineering Chemistry

¹ Annalen, 310, 25 (1900); 319, 59 (1901); 325, 348 (1902).

Another 10 c.c. of milk was next treated by the official Kjeldahl method for casein, and from this result the value of 1 c.c. of N/9 alkali in terms of casein was determined. From a large number of samples the value: 1 c.c. N/9 alkali = 1.63 per cent casein was arrived at. Above is a comparison of some results obtained by the official Kjeldahl method and the new method, using the factor 1.63.

In determining the percentage of casein in a given sample of milk the procedure is exactly as outlined for determining the factor, omitting the Kjeldahl determination. The test occupies only a few moments. It has, of course, the disadvantage that only one sample can be handled at a time, but as a number of samples can be run in a few minutes, this may not prove to be of very great consequence.

From the fact that the chemicals and apparatus required are exactly the same as are in common use in cheese factories, with the exception of the formaldehyde which is very inexpensive, it is thought that the method should commend itself to the serious consideration of dairymen. It is, of course, important that the formaldehyde solution be kept neutral. This may be accomplished by adding a few drops of the indicator solution (phenolphthalein) to the formaldehyde in the bottle, and then adding the alkali until a pink color develops. This fades in the course of time, and the formaldehyde must then be treated again with the alkali.

The proper amounts of indicator (1 per cent solution) and formaldehyde solutions to be used have been found to be about 1 c.c. of the former and 2 c.c. of the latter. An excess of either, however, occasions no error. In the manipulation of the test it is well to add sufficient of the alkali during the first titration to bring the color to a decidedly deep pink, and at the second titration to bring the color to the same shade. The titrations are best carried out in a white cup or porcelain casserole.

If it is desired to estimate the acidity also, the reading of the burette may be taken after the first titration.

The casein is then estimated from the difference between the first and second titrations. Thus both the acidity and the casein are estimated in the one operation. Those dairymen who use N/10 alkali and 9 c.c. of milk as the sample will, of course, employ the same factor. The test is at present recommended for unpreserved milk only, although the author expects to be able to announce a suitable preservative at an early date.

The following table is given for the use of those not wishing to take the time to multiply the amount of alkali used by the factor 1.63:

Cc N/9 alkali used.	Per cent casein.
1.00.....	1.63
1.05.....	1.71
1.10.....	1.79
1.15.....	1.87
1.20.....	1.95
1.25.....	2.04
1.30.....	2.12
1.35.....	2.20

1.40.....	2.28
1.45.....	2.36
1.50.....	2.44
1.55.....	2.53
1.60.....	2.61
1.65.....	2.69
1.70.....	2.77
1.75.....	2.85
1.80.....	2.93
1.85.....	3.01
1.90.....	3.10
1.95.....	3.18
2.00.....	3.26

Instead of using a 10 c.c. pipette for taking the samples and consequently having to multiply the amount of alkali used by 1.63, it is advisable to use a 16.3 c.c. pipette, in which case, the reading on the burette denotes directly the percentage of casein.

A very convenient and simple form of acidimeter has been lately put on the market by the author which may be used for both the "acid test" and the "casein test."

A series of comparative tests, using both the new method and the centrifugal method, has been carried on at the Eastern Dairy School, Kingston. The tests were made independently on the same milks by Messrs. Echlin and Cameron. Mr. Echlin did the work with the new test, and Mr. Cameron that with the centrifugal method. The resulting figures, as can be seen from the following table, are in surprisingly close agreement.

Centrifugal method	New method.	Centrifugal method.	New method.	Centrifugal method.	New method.
2.6	2.64	2.25	2.35	2.2	2.27
2.7	2.69	2.3	2.35	2.4	2.43
2.5	2.44	2.35	2.43	2.4	2.43
2.55	2.61	2.6	2.59	2.4	2.43
2.55	2.61	2.5	2.51	2.5	2.59
2.55	2.61	2.5	2.51	2.45	2.51
2.3	2.36	2.25	2.27	2.4	2.43
2.3	2.36	2.25	2.27	2.4	2.43
2.6	2.61	2.2	2.19	2.45	2.49
2.5	2.53	2.35	2.35	2.5	2.55
2.5	2.53	2.35	2.35	2.3	2.27
2.25	2.28	2.35	2.35	2.35	2.35
2.25	2.28	2.4	2.43	2.4	2.43
2.2	2.20	2.4	2.43	..	..
2.5	2.56	2.35	2.35	..	..
2.6	2.63	2.35	2.35	..	..
2.7	2.67	2.35	2.35	..	..
2.3	2.43	2.3	2.27	..	..
2.3	2.43	2.3	2.27	..	..
2.5	2.43	2.4	2.43	..	..
2.45	2.35	2.4	2.43	..	..
2.56	2.67	2.4	2.43	..	..
2.56	2.67	2.3	2.27	..	..
2.55	2.59	2.25	2.27	..	..
2.55	2.59	..	..	..	..
2.55	2.59	..	..	..	..

The average difference for the above sixty-three determinations is 0.03+.

The Siemens & Holshe Co. of Berlin, is now constructing for a Pennsylvania firm two 20-ton induction furnaces of an improved type that has been developed from the combined patents of Kjellin, Rochling-Rodenhauser and Frich.

The exports of sheep's wool to foreign countries from China in 1912, amounted to 352,977 hundred weight, valued at \$4,048,963 in U. S. currency.

METALLURGY

RUST-PROOFING IRON AND STEEL ARTICLES.*

By EMMANUEL L. BLASSETT, JR.

One of the greatest metallurgical problems of the day has been to produce a non-corrosive surface on iron and steel by chemical or electrochemical methods. The application of enamel, japan, paint, varnish and bronze powders to iron and steel surfaces, to prevent corrosion, is widely practiced. It seems to solve the problem for certain articles, and a description of these methods does not come within the scope of this paper. The real modern problem has been to produce a rust-proof finish that would not obliterate or obscure the minutest outline of the article treated. Furthermore, the ideal process should not destroy the physical properties of the metal, such as its temper and resilience. That the finish should be dark or black in color has also been found desirable in many instances. Nickel has for many years been used as a decorative and non-corrosive coating for iron and steel, but has not proved efficacious or durable enough in this respect. All electro-deposits are apt to wear through in a short time on the edges of plated goods, and when this happens, oxidation rapidly takes place and the rust becoming lodged underneath the deposit soon forces it off. This would not be the case with a finish produced by the latest Bower-Barff process, or by Coslettizing, for the reason that the surface of the metal treated is converted to the black oxide of iron or phosphate of iron. Hot galvanizing has long proved to be a very good protection against corrosion, but its application is very limited owing to its poor appearance and the impossibility of using the process for many articles in ordinary use.

Within the last decade many skilled chemists and metallurgists have sought to discover a chemical or electrochemical process that would protect iron and steel from corrosion, with the result that several new methods have come into industrial use. The processes now in use consist in converting the surface of the article treated to the black oxide of iron, or the phosphate of iron. Further experimenting may result in discovering other iron compounds that may prove equally rust-proof.

BLACK OXIDE OF IRON.

The production of the black oxide of iron (Fe_3O_4) on the surface of iron and steel, to prevent corrosion, has been practiced for many years and is the oldest of the purely chemical methods. The fact that iron became coated with the black oxide when treated with superheated steam was undoubtedly noticed at an early

date. Prof. Barff was the first to seek to apply the principle industrially, but it has remained for later investigators to perfect the methods of producing the black oxide so that it may be used extensively as a commercial finish. There are three processes for producing the black oxide in use at the present time known as the Bradley rust-proofing process, the Bontempi process and the cold process, the latter being used especially on edge tools. When the surface of iron and steel has been converted to the black oxide, corrosion ceases, as no more oxygen can be taken up by the iron. For this reason it forms an ideal rust-proof coating for the underlying metal.

All processes, based upon the use of excessive heat, for producing the black oxide of iron must necessarily have a limited application. Such methods, for instance, cannot be used for finishing edge tools, as the temper would be destroyed. Articles are also enlarged by heating, and measuring instruments and work of delicate design or figures cannot be treated. The black produced by excessive heat is also considered too heavy for some articles, as too great amount of the surface is converted to the black oxide. For edge tools, measuring instruments and articles of delicate design the cold process for producing the black oxide should be used.

BOWER-BARFF PROCESS.

The original process for producing the black oxide of iron by heating the surface of iron to a red heat dates from the year 1876. In that year Frederick S. Barff was granted a patent in England for an "Improvement in Processes for Protecting Iron Surfaces." The original methods employed by Barff and his immediate successors have been greatly improved upon, and a brief historical survey of this process will prove interesting. In the Barff process the articles to be treated were heated to a red heat in a closed vessel, followed by the injection of superheated steam. In the year 1880 George and Anthony S. Bower were granted a patent in England and the United States on a method for "Coating Iron with Oxide." This method consisted of heating the article to be treated in an atmosphere of carbon dioxide, instead of steam. This process was based on the well known chemical fact that when iron is heated to a red heat with carbon dioxide it will reduce the carbon dioxide to carbon monoxide, and the iron itself is converted to the black oxide. Much difficulty was encountered in using both of these methods, and the oxide was apt to scale off and be without uniformity. Several improvements made by Geo. W. Gesner, of Brooklyn, in the year 1888 was the next step in the development of this interesting process. Gesner's modification consisted in

*From The Metal Industry.

introducing an hydrocarbon, such as naphtha, with the steam. The black oxide produced by the Gesner method contained hydrogen, which rendered it less liable to scale. Gesner also improved the furnace for producing this finish. All these early methods had one great disadvantage in industrial operation. Uniformity was not always possible and the red oxide, or ordinary iron rust, was frequently formed simultaneously with the black oxide. The latest improvement in this process was made in the year 1908 by John J. Bradley, of Brooklyn, and is known as the

BRADLEY RUST-PROOFING PROCESS.*

The improved process introduced by Mr. Bradley was patented by him in 1908. By his method a more durable and uniform finish is produced, and what is of still more importance, the red oxide is not formed. It is interesting to note that Mr. Bradley collaborated with Gesner, while the latter was conducting his experiments in producing this finish. By the Bradley process the articles are heated to a red heat in a muffle and hydrogen gas is then introduced. Gasolene in small quantities is also passed in in order to improve the color of the coating. The ordinary muffle furnace is operated and coke is used for fuel. To produce an even finish the article to be treated is first cleaned by tumbling, pickling or sand blasting. Sand blasting is preferred, as it leaves the surface of the article in a more suitable condition for producing the finish. The articles are left in the furnace for an hour or until a sufficiently heavy coating of the black oxide is produced. They are then taken out and allowed to cool and finally oiled with linseed or paraffine oil. The oiling improves the color for decorative purposes. Steel, malleable iron or cast iron may be treated by this method, and the coating produced is very impervious to the action of the atmosphere.

THE BONTOMPI PROCESS.†

The Bontempi rust-proofing process, patented a few years ago, may also be considered as a modification or improvement on the original Bower-Barff process. The Bontempi process consists in heating the article as in the Bradley process and then passing in steam and the fumes of zinc or some heavy hydrocarbon, such as tar or pitch. A very heavy oxide is produced depending upon the length of time the article is treated. The finish is invariably uniform and of a deep black color. It is claimed to withstand corrosion for an indefinite time. Augusto Bontempi, of the Bontempi Company,‡ has recently improved the process and obtained a patent for the use of various substances, claimed to accelerate the formation of the black oxide. As in the Bradley process, a muffle furnace is employed and the articles are heated to 900° F. or more.

COLD PROCESS FOR PRODUCING THE BLACK OXIDE.

The cold process for producing the black oxide of iron can be used with facility on a large variety of goods. It is especially adapted for refinishing edge

tools and general hardware. Although it is used extensively at the present time, it is most likely to be discarded for more simpler and economical methods, and "coslettizing" or some such process may supplant it. There seems to be no record of the origin of this process, but it is known to have been used for many years, especially for finishing gun barrels. The black oxide produced by the cold process is much lighter than that produced by heating in a furnace and is not considered so highly resistant to the corrosive action of the atmosphere. The cold process produces a smooth and full black coating, which does not scale off and is considered sufficient rust-proof for a large variety of goods.

The process has been described by "Ionic" in The Metal Industry for October, 1910, and only a brief description of the process will be given here. The article should be cleaned as if for plating, after which it is coated over with a solution composed as follows:

Water	4 ounces
Alcohol	4 ounces
Ferric chloride	½ ounce

The solution is applied with a sponge to the article to be treated; care should be taken that the sponge is well squeezed out before applying it to the work. Too much solution in the sponge will not produce the desired results. The articles are then placed in a warm, moist atmosphere. For this purpose a chamber heated by steam is employed and the exhaust from the steam coil produces the necessary moisture. The articles are steamed for 45 minutes, when they are removed from the chamber and immersed in clean, boiling water for 15 minutes. After removing from the water bath and cooled, the work is scratch-brushed on a fine wire wheel brush revolving at about 600 revolutions per minute. To obtain a good and durable black oxide, it is necessary to sponge the work with the solution previously given two or three times, followed by steaming, hot water treatment and scratch brushing as in the first operation. After the final scratch brushing the articles are oiled with linseed oil and carefully wiped with a cloth. The oil should always be applied, as it improves and deepens the color and makes the work still more rust-proof. Anyone interested in this process should obtain a copy of The Metal Industry for October, 1910, wherein a complete and adequate description of the process is given.

There are several modifications of this process in which more complicated solutions are employed, but the results are not any better and are usually more expensive to operate, requiring more labor and attention. The following formula is said to be used extensively on Swiss watches and novelties made of steel and iron:

	Grammes.
Nitric acid	27.0
Hydrochloric acid	7.5
Copper sulphate	7.5
Ferric chloride	333.5
Water	2,000.0

The articles are sponged as previously described and placed in a drying chamber heated to about 100°

*The Metal Industry, January, 1912.

†Bontempi Rust Proof Company, Bridgeport, Conn. The Metal Industry, May, 1912.

F. for 20 minutes. The work is then steamed in a separate compartment for a half hour or more and again dried in the drying chamber for 20 minutes, when the work should be coated with ordinary iron rust. The articles should then be immersed in clean, boiling water for 20 minutes, and after being allowed to cool are scratch brushed. These operations as in the process previously described are repeated three three times, or until a suitable black is obtained. This process is said to be extensively used in Europe, but it seems to be more expensive in operation and the results are the same as in the cold process previously given.

OTHER METHODS FOR PRODUCING THE BLACK OXIDE.

There are various other methods for producing the black oxide of iron. It may be produced by immersing the iron or steel article in molten nitre (nitrate of potassium or saltpetre) or nitrate of sodium (chile saltpetre). This is known as steel bluing, and is used extensively on a large variety of articles. The color may be blue or black, depending upon the length of time the article is immersed and the degree of heat employed. Small articles, such as steel buttons and buckles, may be given a black finish by tumbling in a sheet iron barrel heated to the right temperature by means of a gas furnace. This is the usual method for finishing iron and steel novelty work requiring a black finish. Heating the articles in charcoal also produces a blue or black oxide, and the process is extensively used on revolvers and general hardware. These methods, however, do not produce a finish that can be considered rust-proof. The oxide formed is too light and corrosion is not retarded to any great extent.

COSLETTIZING.

The method known as Coslettizing is very simple and economical to operate and may be regarded as the most advanced step in rust-proofing iron and steel. It is the ideal process for general work. Coslettizing consists of producing upon the iron or steel article a coating of phosphate of iron (Fe_3PO_4), which is quite impervious to the action of the atmosphere. This process was discovered by Thos. W. Coslett, an analytical chemist of Birmingham, England. The process was patented in England in 1906 and in the United States in the following year. The process was described by the writer in *The Metal Industry* for May, 1911, and its extensive application since that time merits further attention. It is now extensively used on typewriter parts, harness trimmings and general hardware. There is a very wide field for the application of this process, and articles of the most delicate nature may be treated without injury. This method does not destroy the physical properties of the metal treated, and articles are not perceptibly enlarged as in the heat process. Such articles as watch springs and micrometers have been successfully treated by this method.

The solution for Coslettizing is made as follows:

Concentrated phosphoric acid.....	½ gal.
Water	½ gal.
Iron filing	2 lbs.

When the iron is thoroughly dissolved, this solution is added to 50 gallons of water. A wrought iron tank is necessary to hold the solution, which should be heated close to the boiling point by a gas stove or a steam coil. If desired, the tank may be encased in brick work and wood or coal may be employed as fuel.

The work to be treated by this method is first cleaned as if for plating. If necessary it should be pickled in the usual muriatic dip to remove the rust. The work is suspended in the solution by means of iron wire or hooks; small articles, such as screws or bolts, are placed in iron or earthenware baskets. The solution must be kept close to the boiling point, and the work is allowed to remain in it from one-half hour to three hours, depending upon the nature of the work or the thickness of the coating required. This process produces the most rust-resisting finish for iron and steel by simple immersion in solution that has yet been discovered. A very slight amount of the surface of the article treated is converted to the phosphate of iron, but most of the coating comes from the solution itself. When the solution is working properly, a heavy coating is produced in two or three hours. A convenient arrangement for a small bath is to make up the solution in an enamel or agateware tank and heated by placing it in boiling water. A wooden tank may be used for holding the water, which should be kept hot by a steam coil.

When the work is removed from the solution it should be allowed to dry in the air; rinsing in hot water is unnecessary. If the work treated is to be used for ornamental purposes it should be scratch brushed on a fine wire wheel brush revolving about 600 revolutions per minute. The finish is much improved by oiling with linseed or paraffine oil.

The licensees of this process are given a chemical test worked out by the inventor, which indicates the conditions of the solution and the proper density to maintain it. The manufacturers who are using this process speak very highly of it. Typewriter manufacturers use it on work that is finally japanned and claim that it retards corrosion to a remarkable degree on typewriters used in torrid climates or on vessels. If the body of the typewriter is not Coslettized, the rust eats through the japan much sooner. The inventor of this process has recently patented a new formula for Coslettizing, which contains zinc and is made up as follows:

Zinc	6 ounces
Phosphoric acid	1 pint
Water	1 pint

This is the "stock" solution which should be used in portions of 1 ounce to each gallon of water. An interesting modification of this process was recently patented by F. R. G. Richards, of Coventry, England. The formula is as follows:

Water	1 gallon
Manganese dioxide	3 pounds
Phosphoric acid	½ pound

The English courts declared this formula an in-

fringement on Mr. Coslett's process, and the patentee is barred from introducing it. Coslettizing has now become a firmly established industry, and in the future it will be used extensively on general hardware.

ELECTROCHEMICAL METHODS FOR RUST-PROOFING.

Electrogalvanizing is unquestionably the most durable and practical rust-proof finish that can be produced by electrodeposition. The work to be rust-proof should be given a heavy deposit so that it may not be readily worn off by friction. The solution usually employed is composed as follows:

Zinc sulphate	2 pounds
Aluminum sulphate	2 ounces
Water	1 gallon

A good heavy deposit of brass, copper or nickel on steel and iron retards corrosion for a considerable time and these methods are too well known to describe here. Black nickeling seems to be the only method for producing a black finish directly on iron and steel by deposition that is fairly rust-proof. To produce a black nickel deposit the following formula is generally used:

Double sulphate of nickel and ammonium ..	10 ounces
Zinc surplate	1 ounce
Sulphur cyanide of potash	2 ounces

Black nickel deposits should be lacquered or oiled to still further retard corrosion or prevent staining.

Another method that produces a black finish on iron and steel by the use of the electric current is as follows:

Lead nitrate	12 ounces
Ammonium sulphate	8 ounces
Water	1 gallon

The articles to be colored are hung on the positive or anode rod. For a cathode, sheet steel may be used. This solution merely colors the work treated and the finish should be oiled or lacquered when it will keep from rusting for a certain time. The rust-proofing of iron and steel articles by chemical or electrochemical methods is still capable of further development, and the future, no doubt, will see new processes come into industrial use.

Turkish Yield of Gum Tragacanth.

The U. S. Consul of Mersina reports that the yield of Asia Minor gum tragacanth for 1913 is about 250 tons, of which not over one-third is white and the balance is discolored or of inferior quality. About 100 tons of this gum were exported from Mersina in 1913, principally to France, Germany, Russia, and the United States. There has been a large increase in the exportation of this gum from Mersina to the United States during the past few years. In 1912 such exports were valued at \$8,870, while in 1913 (to Dec. 15) their value was \$19,659. The increase is due to more direct buying from the source of supply and partly also to the decisions under the pure food and drugs act, which prevent the substitution of inferior gums for gum tragacanth.

ELECTRO METALLURGY: THE ELECTRIC FURNACE AND COMPLEX ORES.

In countries with unlimited water power electric smelting of complex ores and the refining of steel has made very substantial progress during recent years; but the opinion frequently expressed that in districts where water power is not available the electric furnace cannot be successfully introduced may be questioned. The objection generally raised is the cost of power, but if the point is carefully considered it is not really so formidable as it at first appears to be. Many power stations can provide power with a high and constant load factor at a cost of two-thirds of a cent per kw. hour; at that price electric smelting may be profitably introduced. The refining of steel and the treatment of complex ores has for some years been successfully effected by the Ruthenburg electric furnace, operated on a three-phase current, of the resistance type. The passage of a low tension current through the bath generating the heat. There are three carbon electrodes, which are protected from the corrosive action of the hot gases by water jackets, which are lined with refractory material in such a way as to avoid arcing between the electrode and jacket wall, even when on occasion the electrode is broken. The furnace attendant is able to raise and lower the electrodes as may be required—they are immersed in the bath, with the water jackets extending nearly to the surface.

No destructive effect is produced on the furnace roof as the electrodes are actually consumed in the heat zone, the whole of the electrodes being used up without waste. This type of furnace, variously modified, is applicable to all classes of steel refining and other analogous processes. When steel has to be refined directly from an iron ore charge, the necessary adjuncts for the introduction of carbon monoxide are fitted. The furnace may be briefly described as follows: The body consists of an iron cylinder lined with ordinary refractory material. Shales from which these can be prepared frequently occur, in many parts of Europe among the coal-bearing rocks, notably in Scotland and Lancashire. Attached to this cylinder is a removable hearth composed of ordinary firebrick and refractory lining, which can be run on a track and used as a ladle without heat loss or skulling and by skillful manipulation metals can readily be poured, which would otherwise be difficult to release by tapping. It is important to note that this type of electric furnace can be kept in continuous operation by the provision of a spare hearth and can be worked for years without repairs being necessary. The design of the furnace is such that every portion of it is accessible and the construction has been simplified to such an extent by prolonged experience that any repairs can be speedily effected.

In smelting ores requiring 1,000 kw. hours per ton in a furnace provided with 24-inch electrodes, with a

voltage of 50, the capacity is 2,075 units an hour, equal to 49,800 per day. If the total number of daily units is divided by the current required per ton of ore, the per diem capacity of the furnace can be ascertained. It has been found desirable in practice to design the furnace hearth with a capacity equal to one-fourth of the furnace's daily capacity. These furnaces have a very high efficiency as regards current consumption, as the thermal losses arising from radiation have been practically eliminated.

Many complex ores are known to exist, which have not been mined, owing to the impossibility or difficulty of successfully treating them. The electric furnaces of the more recent types will give many of them a value they have not hitherto possessed. Both in America and Australia mines have remained undeveloped through that cause. Concentrates which formerly could not be treated have been successfully manipulated by some suitably modified variety of these furnaces, the design of which is the joint work of the electrician, metallurgist and engineer. To quote an instance of a typical complex ore containing at least eight elements. Three of them zinc, lead and sulphur with a small percentage of silver were in the first instance volatilized. A matte was left in the hearth containing copper, iron, gold and silica, also some residual silver. The volatilized metals were caught in the wet condensation chamber with sulphur dioxide to form sulphates of the lead and silver, which being insoluble, were precipitated. The zinc was dissolved in the acid to point of saturation, when it was precipitated in suitable tanks as pure oxide for after-treatment in retorts. The silver-lead precipitate was afterwards sweated into bullion. The copper-gold-silver-iron matte was then ready for direct treatment in the copper smelter, where mixed with siliceous ores the iron was fluxed out, leaving the purer matte for ordinary treatment.

Electric smelting facilitates the production of ferro alloys, of which ferro tungsten is one of the most important. Tungsten steel, now extensively used for a variety of purposes, is being produced in annually increasing quantities. Ores containing tungsten can now be economically smelted by electricity, even in countries where water power is not available. Material with one-half per cent of carbon is the grade usually produced, but even a more minute percentage is possible. The phosphorous and sulphur content is exceptionally low when precautions are taken in the selection of the raw materials. The ferro tungsten ores are smelted with a suitable reducing agent and fluxes to produce the alloys, in a specially contrived electric furnace. The alloy produced is generally graded, the tungsten ranging from 70 to 85 per cent, the remainder is iron. It is occasionally found that a smaller percentage of tungsten, approximately 50 per cent, is even more suitable for the production of large quantities of tungsten steel in one charge. It is now well established that tungsten and iron, 50 per cent of

each, form a true chemical compound and not merely a physical mixture, comparable to carbon in pig iron. When, however, tungsten is present in quantities above 50 per cent, say 60 or more, a physical mixture only is produced. It is an essential point for the production of the alloy that the iron used must have a high standard of purity. An alloy with 50 per cent of tungsten has a relatively low melting point. The output with a higher percentage of tungsten has to be treated in a steel bath with a considerably higher temperature in order to be dissolved properly; an important point in the process, for if the alloy should not be thoroughly dissolved, the tungsten may produce flaws in the bars turned out, which of course depreciate the value of the steel.

With careful supervision a power consumption of 4,000 kw. hours per ton of metal should suffice to produce the best grades of ferro-tungsten. The power may be supplied at 500 volts d.c., which could be converted into alternating current of low voltage by means of an ordinary motor generator set, provided with suitable regulating devices. The ore may be ground in a ball mill and mixed with the reducing agent and flux in the necessary proportions and fed into the furnaces. As soon as the smelting has been affected, the blocks of metal produced can be removed with the aid of a crane and broken up; the large fragments can be cleaned and reduced to "walnut" size, then sorted, when they are ready for sale. Ferro-uranium as well as ferro tantatum are possibilities of the near future.

Electric smelting can also be applied to tin ores. The process has the advantage over that hitherto used, that wastage is very considerably reduced, if not practically eliminated; an important point when the value per ton of the output is so high. Up to the present time tin ores have been treated in coal fired reverberatory furnaces, also in shaft or blast furnaces, extremely crude appliances compared with the most recently devised electric furnace. Hitherto the losses of metal in the slags and by volatilization have probably been as high as 7 to 8 per cent and even when the slags are treated a second time the loss may average 5 per cent. These crude furnaces have also the disadvantages that they can only be intermittently in use and that a certain percentage of impure alloys of tin are produced. These and other drawbacks are eliminated by the substituting of the electric furnace.

No combustion can take place in the electric furnace and as it is practically closed no losses from volatilization are possible. The tin contained in the slags produced by the electric furnace are almost negligible in quantity, as low as 0.25 per cent in exceptional cases. The best results have been obtained by working electric furnaces in series or couples. The first may be charged with ore and worked to yield a large output with a slag containing 15 or 16 per cent of tin, which is then treated in the second furnace, before it is

cooled, resulting in a slag with only traces of tin. Lead ore and tin ore may be worked together to produce tin solder. The power consumption per ton of tin should be very considerably below 2,000 kw. hours. Electric smelting plants are worked continuously day and night for months, an important advantage over the systems they are supplanting.

Some years ago an electric furnace was erected near Shasta for the direct production of pig iron from the ore by electric smelting. Great difficulties were met with, but they have now been overcome, and it is possible, as the result of prolonged perseverance, to put a commercial product on the market. The chief constituent apart from iron and carbon is silicon, as only traces of sulphur and phosphorus occur. The silicon varies from 5 to 1 per cent and the output is graded according to the silicon percentage into twelve grades.

THE SLAGGING GAS PRODUCER.

In a paper presented at the fall meeting of the American Institute of Mining Engineers Mr. William H. Blauvelt, Syracuse, N. Y., discusses the advantages and disadvantages of the slagging gas producer. His paper, practically in full, follows:

The advantages and disadvantages of the slagging gas producer, together with some historical facts, were presented by William H. Blauvelt, Syracuse, N. Y., at the fall meeting in New York of the American Institute of Mining Engineers in a paper substantially as follows:

The type of gas producer in which the ashes are fluxed and run off as slag was among the very earliest made. Ebelman built the first one in 1840 at Audincourt, France, only a year after the installation of the first gas producer of which we have record. Charcoal was used as the fuel, with blast-furnace slag and clay as flux. My interest in this type of producer began when as a boy I saw the fluxing producer at Chester, N. J., which was invented by W. J. Taylor, and described by him in 1881. This producer was invented independently by Mr. Taylor to meet the difficulties he experienced in making producer gas for roasting sulphurous iron ores.

It will be of interest to review briefly his description of his producer. It was built like a small blast furnace, having a hearth 24 in. in diameter and 24 in. high. The bosh angle was 25 deg. from the vertical; the diameter of the bosh 4 ft. and at the top 3 ft.; the total height 12 ft. The producer contained one water-cooled tuyere 12 in. above the bottom, with a 1½-in. nozzle; depth of the coal above the tuyere, 6 ft. Mr. Taylor mixed the coal with from 30 to 40 per cent of basic blast-furnace slag to flux the ash. Occasionally some limestone was also used, but never limestone alone, as the use of the furnace cinder gave a larger volume of slag and made it easier to maintain a proper fluidity. The producer was blown with

a small Weimer blowing engine, delivering 300 ft. of air per minute, at from 1 to 1.5 lb. pressure. The slag was tapped every 2 hr. and was black and glassy in appearance. Broken or egg size anthracite was used. The fine sizes of anthracite could not be made to work. Mr. Taylor expressed the belief that bituminous coal could be used if not too fine, but no experiments were made with this coal. Runs were made of four weeks' duration, with no stops or changes. Mr. Taylor reported the following advantages:

1. Excellent gas, very uniform in quality. The high fuel bed permitted no air to pass unconsumed, and the gas was almost entirely free from carbonic acid.

2. No cleaning of the producer to remove ashes, so no waste of coal and no cessation or irregularities in the flow of gas.

3. Quantity of gas easily controlled, and "any-one familiar with blast-furnace practice can run it, particularly if cinder for fluxing is available."

The power required for blowing the producer for gasifying 200 lbs. of coal per hour was 1.5 h.p., or, assuming 3 lbs. of coal per h.p., 2.25 per cent of the coal gasified. This consumption of steam compares favorably with ordinary producers, but the rate of gasification, about 16 lbs. per sq. ft. per hour, was not remarkable for the size of fuel used. Mr. Taylor did not continue the operation of the fluxing producer, mainly on account of the skilled attention required in its operation. A man "familiar with blast-furnace practice" is often not available for the operation of producers. The high pressure of blast used and the necessity for employing a blowing engine were also among the disadvantages. He did not state why only the larger and more costly sizes of anthracite could be used, but at present comparative prices this would be a serious objection.

There appears to be no further record of experiments with the slagging producer until within the last few years. A battery of "S. F. H." slagging producers was installed at the glass works at Gironcourt in 1907, and this plant is reported to be still in operation, furnishing gas to the glass works. In the report of the operation of this plant there is no reference to the type of flux used, but it is reported that all kinds of fuel are successfully gasified, no matter what the content of ash, the only necessity being that the fuel contain sufficient fixed carbon to develop heat to gasify the carbon and fuse the ash. It is claimed that the heat required to fuse the ash is much less than the equivalent of the carbon lost in the ash of ordinary producers. One coal containing from 20 to 25 per cent of ash gave a gas containing from 2 to 3 per cent of CO₂, 28 to 30 per cent of CO, and 9 to 10 per cent of H₂ and CH₄.

The most recent work done with the slagging producer is that described by the Bureau of Mines, Technical Paper No. 20. This work was done at the

Pittsburgh Laboratory of the Bureau, with a view to determining the value of this type of producers for utilizing low-grade fuels. It does not appear from the report of these tests that the slagging producer gives results essentially superior to other types of producers for gasifying low-grade fuels. The experiments at the Coal Testing Plant of the Bureau at St. Louis in 1903 and 1904 showed that fuels containing very high percentages of ash could be successfully gasified in producers of the ordinary type.

The report of the Bureau of Mines does not give the dimensions of the producer used, but six air tuyeres were employed, and in addition four separate steam tuyeres located above. On account of the extremely high temperatures it was found necessary to provide pipe coils in the brick lining for water cooling, and magnesite brick was used between the coils and the fire. The cooling coil extended over a space of 20 in. above the air tuyeres. The blast pressure used was from 5 to 16 in. of water, and it was found advantageous to pre-heat the air to about 440 deg. F. Steam was employed at times up to 0.75 lb. per pound of fuel gasified, and it was found that this produced no chilling effect on the slag, as the steam was introduced above the point of highest temperature. It was found difficult to operate this type of producer intermittently without trouble from the chilling of the slag, so it does not appear that it would be satisfactory in cases where gas is required only in the day time, for example. The analysis of the gas showed high CO and low CO₂ content, the latter being as low as 1.5 per cent, but no analyses are reported showing the effect of steam on the composition of the gas.

The experiments developed a number of difficulties in the fluxing of the ash, and it was found that the theoretical percentage of limestone was not nearly sufficient to produce a fluid slag. Frequently large quantities of fine ash blew over with the gas, "because of the heavy air blast," and probably some of the limestone was blown over with it. One occasion is reported where practically all of the ash and limestone escaped in this way. Comparing the air pressures reported with those used in producers of the ordinary type, it would be interesting to observe, in further experimenting, if a careful proportioning of the depth of the fuel bed to the rate of combustion would reduce the trouble from this source.

When the conditions were right and the operation of the producer was maintained continuously there was no trouble in tapping off the slag in a satisfactorily fluid condition, and in maintaining a uniformly high quality of gas. The bureau has been carrying on experimental work since the publication of the above report, and we hope to have before long the results of this additional work.

The latest work with the slagging producer is described in a French patent issued to E. Servais, January 21, 1913. In this producer there are two sets of tuyeres, one set arranged just above the fire

zone and supplied with steam or gas to reduce the temperature in the fuel bed by its decomposition. A second set of tuyeres is arranged just below, through which the air blast is admitted. These tuyeres are set in an eccentric ring, in order that a whirling movement may be given to the air in order to agitate the molten slag in the crucible. The inventor claims that this rapidly melts down any solid lumps that may form. A combustion chamber is arranged beneath the crucible in which a mixture of gas and air may be burned to help in maintaining the temperature above the fusing point of the slag. In operating this producer the fuel is sprayed with lime water, or mixed with a suitable amount of basic blast-furnace slag.

The work done thus far with the slagging producer does not indicate that the problem has been thoroughly worked out, and there is much experimenting to be done before this producer can be put on a commercial basis. The increasing cost of the higher grades of fuel, and the large amounts of low-grade fuel that are available in almost all parts of the country, make the perfecting of a producer that will successfully gasify these low grades a most interesting and important problem.

There is one field where the slagging producer would have material advantages. It would be ideal for gasifying coals having a fusible ash. No matter how badly the ash might clinker in an ordinary producer, it would have no terrors for the slagging producer; in fact, the more fusible the ash, the better. Such coals are ordinarily gasified with the use of an excess of steam, which is not only costly to generate, but injurious to the gas, as much of it passes through undecomposed. There are many of these clinkering coals which are objectionable in the ordinary gas producer, and if the slagging gas producer can be worked out so that the cost of operation is about on a par with other types, it will find a field of usefulness waiting for it.

A REVIEW OF STEEL RAIL CONDITIONS.*

By C. W. GENNET, JR., '98.

The last fifteen years have witnessed many changes in matters involving the manufacture and use of steel rails, the more important of which it seems opportune to mention; and especially perhaps, because, of all engineering subjects, steel rails is one of the least mentioned in modern text books.

Prior to 1900, Bessemer steel was by far the kind most commonly rolled for general purposes, although open hearth steel was consistently used for important structural sections, plates, axles and heavy forgings. The thought of rolling open hearth steel into rails on a wholesale basis, so to speak, had received scant attention, for while it is true that some such rails were in service their advantage if any, had not been demonstrated, nor had the approaching necessity of conserv-

*From the Sibley Journal of Engineering.

ing Bessemer ores and using basic ores more freely been seriously considered. In 1899 over two and one quarter million tons of Bessemer steel rails were rolled and only 523 tons of open hearth. It was about this time, or a few years after, that the pioneer open hearth steel rail plant began operating in the south where conditions imposed by the chemical composition of the Alabama ores demanded use of the open hearth process, and the production of rails rolled from such steel thereby received a considerable impetus. The Southern rail lines found it, of course, financially economical to lay the open hearth rails because of the geographical location of the mill and the consequently cheaper freight rates necessary, and other northern lines at once began experiments aiming to prove whether or not any increased life was obtainable by the use of open hearth in lieu of Bessemer rails.

It has been the unanimous opinion among engineers for many years that the phosphorous content of Bessemer steel for rails, and in fact for most other products should not exceed one-tenth of one per cent. The great ore deposits of the Lake Superior district are largely what is termed the basic grade, that is, the phosphorus content is too great in the ore to permit of its reduction in blast furnaces and final conversion in Bessemer converters and then be less than 0.1 per cent in the finished steel. Because of this scarcity of domestic Bessemer ore it has been found impossible to continue the manufacture of Bessemer steel in the same proportional amount of total production as formerly and the complexion of the whole field of steel making has therefore been changed to conform to the recognized conditions. The continued and rapid upgrowth of the open hearth steel industry in the United States is best shown by the following figures:

Year—	Bessemer ingots, gross tons.	Open Hearth ingots, gross tons.	Total ingots, gross tons.
1900	6,678,303	3,220,644	9,898,947
1905	10,919,272	8,444,836	19,364,108
1906	12,243,229	10,260,522	22,503,751
1907	11,634,276	10,803,211	22,437,487
1908	6,096,196	7,524,952	13,621,148
1909	9,296,969	13,892,896	23,189,865
1910	9,354,437	15,641,158	24,995,595
1911	7,890,753	15,027,459	22,918,212
1912	10,259,151	19,909,875	30,169,026

The rolling of open hearth steel rails has kept pace with the increased production of open hearth steel for the now quite obvious reason, and figures showing the decline of the Bessemer rail and the upgrowth of the open hearth are interesting:

Year—	Bessemer rails, gross tons.	Open Hearth rails, gross tons.	Total rails, gross tons.
1900	2,383,651	1,333	2,384,987
1905	3,192,347	183,264	3,375,611
1906	3,791,459	186,413	3,977,872
1907	3,380,025	252,704	3,632,729
1908	1,354,236	567,304	1,921,540
1909	1,767,171	1,256,674	3,023,845
1910	1,884,442	1,751,359	3,635,801
1911	1,053,420	1,676,923	2,730,343
1912	1,099,926	2,105,144	3,205,070

The change from Bessemer to open hearth steel for rails has been accepted with much general favor. It has resulted in the ability to reduce the influence of the

poisoning element, viz.: phosphorus, to an almost negligible item and thousands of tons of rails are now in service containing less than 0.02 per cent of this harmful event. This decrease in the phosphorus content has made it possible to increase the amount of carbon in the steel, and, as carbon is one of the most important life giving elements to rails, the result has been in the direction of increasing the life of rails. For the sake of comparison the specified chemical composition of typical rails is given:

	Bessemer Steel 100-lb. rail of 1900.	Open Hearth Steel 100-lb. rail of 1914.
Carbon, per cent.....	.45 to .55	.63 to .76
Phosphorus, per cent	Not over .10	Not over .06
Manganese, per cent.	.80 to 1.10	.60 to .90
Silicon, per cent.....	Not over .20	Not over .20

In 1900 there were no physical tests consistently made on the rail rolled. The art of Bessemer steel manufacture and rolling was often regarded as under such perfect control that the product was of necessity accurate, provided the chemical composition specified had been complied with, and several millions of tons of rails were made on which there were actually no tests, although in many cases purchasers did demand that an occasional representative rail be submitted to the recognized drop test. In later years, however, the importance has become appreciated of regarding each heat cast for rails as a unit unto itself, and drop tests are made regularly on a piece of rail from at least one ingot from every heat of steel and frequently on three such pieces. In fact the present tendency is to increase the number of test pieces and ultimately no doubt a piece from every ingot rolled will be subjected to careful tests.

These drop tests generally consist of taking a length of rail about five feet long from the top of an ingot where segregation and piping are most likely to be found, and subjecting it to the impact of a weight of 2,000 pounds falling from a free height of from sixteen to eighteen feet and striking the test piece on the head, or base, midway between the supports on which it rests, three feet apart. Under this blow the test pieces bend and take a maximum set of from one and one-half to two and one-half inches in the three feet. If the metal or its treatment is defective in some respect the test pieces may be broken by the blow of the tup, in which event it is necessary to make various re-tests in order that the rails represented may be accepted. Frequently under certain current specifications the test pieces which may have resisted the blow successfully must be nicked and broken in order that the condition of the fractured metal may be examined, and based upon its condition the rails represented are accepted or rejected.

In short, while 15 years ago the chemical composition of steel was the principal feature of rail specifications, today we have stringent and difficult tests with which the rails must comply prior to their acceptance, and the probability before mentioned, is that the number of these tests will multiply as time goes on.

This increased testing can be largely attributed to the growth of open hearth rail manufacture. Bessemer heats of steel weighed from 10 to 15 tons and were cast into comparatively small ingots making three or four rails. Open hearth steel of the present day is made in heats weighing 100 tons and then cast into say 25 ingots each making from 6 to 8 rails. Inability to control the complex chemical reactions occurring in open hearth furnaces as effectively as those in Bessemer converters is unquestioned. This condition results in the steel varying within comparatively narrow limits of chemical composition but nevertheless often varying to an undesired degree; while, in addition, the larger ingots generally cast of open hearth steel invite greater opportunity for the inevitable effects of piping and segregation. Hence it becomes of the utmost importance that a comprehensive system of testing be prescribed and rigidly enforced in order that the product be proved absolutely safe.

While manufacturers of rails have been adapting themselves to the new methods, railroads have been busily engaged in perfecting their share of the responsibility for meeting the demands of transportation facilities. My thesis drawing was a section view of one of the famous family of locomotives of the New York Central system to which No. 999 belonged. It represented the height of passenger locomotive development of that day. No. 999 hauls a milk train now on a branch line and the "20th Century Limited" is drawn by a motter weighing 50 per cent more than it did and subjecting the rails to a correspondingly increased impact. The same conditions have occurred on every important railroad, viz.: a tremendous increase in the weight of motive power and rolling stock, and to which should be added the frequency of trains. Obviously the weight of the rail section has had to be increased to meet this condition, and where 80 or 85 pound rails were common, 90 and 100 pound rails are rapidly replacing them and there are cases of rails weighing 120 and 135 pounds per yard being laid in special places.

In 1893 the American Society of Civil Engineers recommended certain sections of rails, which have since borne that name, and which quickly came into very common use. These sections had 45 per cent of the metal in the head, 21 per cent in the web, and 37 per cent in the base. This unequal distribution introduced many complications, the most important being that in order to accurately form the thin flanges the bar had to be rolled at such a high temperature that the head metal was of coarse crystalline structure; while, also, the thin flanges would crack off in the stress of service, forming the well known crescent or moon shaped breaks and usually causing very soon afterward complete fracture of the rail. So much agitation ensued that finally in 1908, through the instrumentality of the American Railway Association, new sections, which bear their name, commenced to be rolled. These "ARA" sections are of two types, one of which emphasizes the importance of the rail as a girder and contains slightly more metal in the base

than in the head. Because of its stiffness and design this section is highly satisfactory for the long stretches of high speed track existing on prairie lines. The other section is much less stiff and contains practically the same amount of metal in the head as in the base. Both sections permit of rolling easily and accurately to template, and because of the nearly equalized design, the steel is much improved in its crystalline structure. Use of the new "ARA" sections has resulted in a marked decrease of broken rails and needless therefore to say the success of the new sections have been most welcome.

In spite of the changes already recorded, manufacturing and service conditions have been by no means perfect and the large number of broken rails occurring in the extremely severe winter of 1912 brought forth state and governmental investigations and activities aiming to relieve the situation and make transportation facilities less hazardous. Of interest in this connection was the inauguration early in 1912, of a system of special inspection of the manufacture of rails. Perhaps it has not been generally known that, ever since the first rail was rolled in this country, practically every rail made has been subjected to a most careful scrutiny prior to shipment by an inspector representing the purchaser. But this inspection usually has been confined to the finished rails, and, in particular, to their freedom from certain defects of a physical or mechanic nature. Little, if anything, was known by the purchaser of the history of the manufacture of the steel and its subsequent rolling; all of this being left to the integrity of the manufacturer, who often invited the "cutting of corners," so to speak, in the desire to get out the tonnage, by paying his workmen on a tonnage basis. The plan of special inspection which was established provided for the placing of responsible inspectors in the various departments of the steel and rolling mills. Their duties consist of observing and recording every important phase of manufacture, all of the data being compiled for future use, in order, for example, that the complete history of a broken rail may be available. As was expected, the presence of an inspector in the various departments has had a great moral influence on the workmen, and as manufacturers have heartily co-operated in the general movement the results from the plan of special inspection have been recognized as a most important achievement.

The problem of the steel rail for the American railroads has by no means been entirely solved, new demands and complications coming rapidly. Steel made by electric furnaces, and various alloy steels as manganese, titanium and vanadium are all being urged as metallurgically capable of improving conditions, generally by affording a better wearing rail and one less likely to be broken. On the whole it is difficult to predict what may happen in the next 15 years, but indications are that no changes will be brought about as great as those which occurred in the manufacturing practice and use of steel rails in the last 15 years.

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HARRY McCORMACK, Editor.

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NOTES AND COMMENTS.

Plantation Rubber In Cochin China.

At the request of this consulate the Director of the Agricultural and Commercial Service of Cochin China prepared a detailed statement showing the status of rubber cultivation in this section of French Indo-China. From the data supplied by him it appears that there are in Cochin China 494,200 acres of land thought to be suitable for Hevea rubber, of which 168,000 acres have been taken up. Of this latter area, 29,652 acres are actually under cultivation, the plantations having an aggregate of 3,800,000 trees.

With the exception of the Belland Estate (Government experiment station), covering 123 acres and having 15,000 trees, the estates are not producing on a commercial scale, and it is therefore impossible to compare the local industry with that of the neighboring Straits Settlements and Ceylon, where rubber cultivation is further advanced. However, it is the opinion of some experts that the soil and climate of Cochin China are not so well adapted to the Heveas as in the Straits and Ceylon, and that the same yield per tree cannot be obtained.

The average age of the Cochin China trees is $2\frac{1}{2}$ years. It is estimated that on the basis of the present planted area the production of rubber in this territory in 1920 will be between 3,500 and 4,000 metric tons (metric ton = 2,204.6 pounds). In 1912 Cochin China exported but 72 tons.

Spring Meeting of the American Chemical Society.

The 49th General Meeting of the American Chemical Society will be held in Cincinnati, O., April 8-11, 1914. The officers of the local section are: President, F. W. Weissmann, 2900 Vine St., Cincinnati, O., and Secretary, Stephan J. Hauser, 1623 Maple Ave., College Hill, Cincinnati, O. The titles of papers should be sent to the Secretary, Charles L. Parsons, Box 505, Washington, D. C.

The following chairmen of committees have been appointed:

Executive Committee—Frederick W. Weissmann.
Finance Committee—Archibald Campbell.
Transportation and Excursions—Gordon Farnham.
Press, Publicity and Printing—C. T. P. Fennel.
Reception and Registration—J. W. Ellms.
Ladies' Reception—Mrs. J. W. Ellms.
Entertainment—Richard Lord.
Smoker—F. C. Broeman.
Banquet—L. W. Jones.
Meeting Places—John Uri Lloyd.

Bureau of Standards' Analyzed Samples.

The Bureau of Standards, Washington, D. C., is prepared to issue a sheet brass of the following composition, approximately:

	Per cent.		Per cent.
Tin	1.0	Zinc	27.0
Lead	1.0	Iron	0.3
Copper	70.3	Nickel	0.5

The fee, payable in advance, is \$3.00 per sample of about 150 grams weight.

Sulphur Output and Exports From Sicily.

The U. S. Consul at Palermo, Italy, states that according to the official report of the Consorzio Obbligatorio per l'Industria Solifera Siciliana of Palermo (Compulsory Sicilian Sulphur Combine) for the seventh working year from August 1, 1912, to July 31, 1913, the total production of sulphur in Sicily was 351,752 tons, against 366,457 tons in 1911-12 and 391,908 in 1910-11. These figures show a gradual decrease during the past two working years, the production declining by 25,451 tons in 1911-12, as compared with that of 1910-11 and by 15,489 tons in 1912-13, as against that of 1911-12.

The failure to reach a normal production of 400,000 tons, as it was anticipated, or at least that of the working year 1910-11, which was 391,908 tons, is again attributed to the general conditions pointed out in this consulate's report published in Daily Consular and Trade Reports for November 6, 1911, and to the closing, in 1913, of 7 mines in addition to the 16 mines closed in 1912.

The total sales during 1912-13, including sales for future delivery, amounted to 497,246 tons, against 603,255 tons in 1911-12 and 816,818 tons in 1910-11. On July 31, 1913, there remained to be delivered on sales made 589,477 tons, of which 249,783 tons were

booked for delivery during 1913-14 and 339,694 tons during the following years.

The total exports declined from 447,638 tons in 1911-12 to 434,473 tons in 1912-13, as shown by the following table:

Countries—	1911-12, metric tons.	1912-13, metric tons.
United States	7,125	1,792
Africa	13,327	16,175
Australia	12,648	13,944
Austria	37,265	34,543
Belgium	12,152	12,399
British Indies	4,928	5,342
Canada	16	376
Central and South America.....	7,440	7,624
Denmark	836	305
France	112,897	79,927
Germany	28,869	35,091
Great Britain and Malta.....	20,764	17,540
Greece	14,762	14,606
Netherlands	12,625	12,518
Norway	3,738	9,016
Portugal	14,185	14,758
Russia	22,838	27,358
Southern Italy	78,954	82,348
Spain	6,952	7,036
Sweden	25,339	28,771
Turkey	834	5,186
Other countries	9,144	7,818
Total	447,638	434,473

Niter In Montana.

Last year R. W. Richards, of the United States Geological Survey, visited a niter deposit on Camp Creek, near Melrose, Mont., said to have been discovered by F. C. Moore, of Melrose. While the deposit may not prove of economic importance, it is interesting in that it affords another example of a nitrate deposit in a region having a fairly abundant rainfall.

The value of the deposit cannot be safely estimated from the data which have been collected. Further exploration is needed to determine whether or not the potash and soda nitrates are included in the limestone back from the outcrop. As the average soluble portion of the samples collected by Mr. Richards is only about 1 to 5 per cent, it appears that about 35 tons of rock would have to be treated to obtain 1 ton of the crude salts. This quantity if refined would yield about 440 pounds of soda niter and about 790 pounds of potash niter, the former being at present worth about \$24 and the latter about \$41, making a gross yield of about \$1.80 per ton of rock treated. Better returns might be obtained by treating the loose rock fragments which lie at the base of the cliffs, but such material is very meager in amount.

WANTED—Analytical balance and some apparatus for cash, or will exchange for 3A kodak, typewriter and violin. Must be bargain. Box 17, care Chemical Engineer.

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No. 3.

DO BUSINESS MEN KNOW WHAT A CHEMIST REALLY IS AND WHAT HE CAN DO FOR THEM?

Under the above heading the membership committee of the Chicago section of the American Chemical Society has been circularizing the firms in Chicago and vicinity who are likely to have chemists in their employ.

Some of the points in their circular are so well taken that we venture to present them to the chemical profession as a whole.

It seems as if some such campaign of education might yield results in any of the industrial centers where there are numerous employers of chemists and chemical engineers.

This campaign has been conducted not so much with the idea of the immediate returns in new members as it is with the idea of placing the profession before the employer in the proper light.

The very decided views of some managers that their business could not be so successfully and profitably run without the chemist and the equally positive assertions by others (fortunately not now so common as formerly), that chemists are entirely superfluous, cannot fail to convince an inquirer that there is yet in some places a misunderstanding as to the value of industrial chemistry.

In many lines of manufacture, chemistry is the basis of the processes employed and operation is impossible without its constant application; in some other lines operation is possible, but competition admittedly could not be met without proper chemical control and the security and profit resulting from it; there are many others in which the chemist has only in isolated cases been recognized and allowed a hand so far, but which eventually will turn to him for aid and regret that it had not seen the light sooner. Not only in manufacturing has the chemist become a necessity, but also in trading and other lines of business where the great mail order, wholesaling and retailing firms are using him to safeguard the quality of goods purchased and sold. The past twenty years has witnessed a greatly increased recognition of the chemist as a necessity in many new lines of business and this is only the beginning.

It is unfortunate for both the business man and the

chemist, and for chemistry as a profession that in many cases there is not yet a proper understanding of what the chemist can or should do. Considerable of this misunderstanding is attributable to the chemists themselves. Too often the graduate just out of school does not realize that he has only acquired the "A B C's" of chemistry as far as practical application and industrial problems are concerned. He often attempts without any practical experience to fill a position in which only an experienced and high grade man could succeed. Of course, for routine analysis a well trained yet inexperienced man may do well enough, but where interpretation of results is concerned, and, especially where application of chemical principles to practical problems is demanded, experience is necessary unless sufficient time and opportunity can be given him during the progress of the work to acquire this experience in the plant.

Too often, however, the well intentioned manufacturer hires a chemist without the requisite training and experience, or one whose experience has been in a totally different line. Sometimes when he gets a capable chemist, he does not get satisfactory results because he fails to appreciate that the chemist's work must be done in, what may seem to the uninitiated, a peculiar way, and that real co-operation is necessary. Though a good business man, he himself usually knows little of chemical principles or their application and if his chemist does not produce a certain result and profit each and every hour, as a machine or his clerks will do, he is likely to become dissatisfied and give up without a real trial. Chemical work can be done on a "so much result per hour" schedule only after it has become routine. The pioneering work must be cautiously and methodically done so that shop routine, output and quality of the product shall not be adversely affected during experiments and subsequent substitution of methods or materials. The progressive employer will see, first of all, that the chemist is given a chance to get a practical grasp of the methods of manufacture used in the plant so that he can apply his chemical principles to bring about improvement in quality and reduction in cost by the selection of better adapted yet cheaper materials or substitution of new and more economical processes. Proper analysis and inspection will also prevent the manufacturer receiving poor qual-

ity goods of any kind while paying for and intending to buy high grade goods. System and process engineering are so common and so well known today that no discussion is necessary.

As an illustration of how easily misconception can and has come about, we may cite the case of a foundry owner who had understood that a chemist might help him to make a more uniform, less expensive, yet better product. Happening to know at the time that a young man, the son of a neighbor, had just finished a university course in chemistry, he called him in. Like many new-fledged chemists who have little realization of what they are up against, the young man accepted a small salary with alacrity, plenty of confidence and the best of intentions, fitted up a laboratory in the plant and started his work. He took his analyses with pride to his employer. "But," said the foundryman, "now that I have the analyses, what do I do with them? How can I tell from these how to make better and cheaper castings?" The newly graduated chemist was at the time unable to say. Chemistry consists in more than merely analyzing samples. In order to accomplish the foundryman's intentions and hopes in hiring him, he must have known considerable of the foundry business. To have secured one who could have made the kind of iron desired, pointed out brands of pig iron and other materials that would have been more economical, while still maintaining or improving the quality of the castings, the foundryman should have selected a chemist of experience in the foundry business, i. e., a metallurgist.

He chose the alternate course, however, and gave the young man opportunity to learn conditions and the methods of manufacture used in the plant and time to study and apply tests and remedies. The young man had the requisite fundamental training, the adaptability which should and usually does result from such training, the common sense, "stick-to-it-iveness" and pluck to work hard and learn, and the tact to get along with the men. It required a little time to do it, but satisfactory results were ventually obtained and the product brought under chemical control. Had this business man given up at once, as has too often been the case, when his \$75 a month chemist failed to accomplish in the first month what a \$200 per month chemist should have been engaged for, he would have lost the benefits of chemical science in his business, and for years after said that he had tried it, but chemistry was of no use in his factory.

Now a possible tentative classification of chemists employed in technical work might be:

A. Analysts—those who know how to make chemical determination but whose practical experience has been meager and insufficient to admit of their interpreting their results or of properly applying them in a practical way.

B. Chemists—those who have specialized in chemistry and have mastered the principles so that they can

devise methods applicable to analysis of samples at hand and who have ability to interpret and apply the results to the problems at issue. They should be capable of doing and directing research work.

C. Chemical Engineers—those who have specialized in engineering, but have had enough chemistry to give them a broad grasp of the vital principles and processes of chemistry, chemical and metallurgical industries. They should be sufficiently at home in the branches of engineering so they can design apparatus and plants working with chemical processes and superintend their construction and operation.

The chemist very often develops into the chemical engineer during the ordinary course of his work, getting the engineering knowledge from his association with the practical men and experience with the machinery of the plant. Vice versa, the new chemical engineering graduate sometimes finds a less practical line of chemistry more to his liking and elects to make some branch of straight chemistry his life work.

It is, of course, impossible to give any classification that is satisfactory and applicable to all cases, but the above will do to give a basis of valuation from which the manufacturer can judge of his need and a proper man for his purpose. Such an understanding would have averted many of the disastrous experiences of well intending business men and chemists and much earlier brought to business the benefits which the proper application of chemical principles has given and will still more extensively give.

MAURITIUS SUGAR STATISTICS.

The latest estimate of the Mauritius sugar crop for 1913-14, according to Consul James G. Carter, Tamatave, Madagascar, places it at 245,000 metric tons, as compared with 225,000 tons in 1912. The sugar received in Port Louis from August 1, the beginning of the season, to December 12, 1913, amounted to 175,400 tons, or 2,280,272 bags, weighing from 170 to 179 lbs. each, against 161,475 tons, or 2,099,174 bags, for the corresponding period of 1912. The sugar in store on December 12, 1913, amounted to 1,238,550 bags, against 683,241 bags on December 13, 1912.

Exports of sugar from August 1 to December 12, 1913, amounted to 77,270 metric tons, as compared with 95,054 tons for the corresponding period of 1912. During this period India took 54,004 tons in 1913 as compared with 64,610 tons in 1912; South Africa, 7,197 tons in 1913 as compared with 5,285 tons in 1912, and the United Kingdom 6,361 tons in 1913 as compared with 5,833 tons in 1912.

Prices have been low all the season, opening at \$2.28 per 100 lbs. for ordinary quality Bombay crystals and rising rapidly to \$2.50 per 100 lbs., owing mainly to large forward sales and exceptionally slow arrivals of sugar in Port Louis. The market on December 17, 1913, was very weak, and sugar was selling at the lowest figure on record, \$2.18 per 100 lbs.

THE MANUFACTURE OF BY-PRODUCT COKE.*

T. V. SALT.

Before going into the process of the manufacture of coke, it would perhaps be desirable to point out for the benefit of those who are not familiar with the subject, a few of the economic and commercial aspects, the present status and future possibilities of the by-product coke industry.

Coke is the residuum of a coking coal after the latter has been subjected to the process of distillation of high temperatures. The process of distillation is carried out in two ways: In beehive ovens with only partial exclusion of air; and in by-product coke ovens and gas retorts with entire exclusion of air.

In the beehive type of oven, the coking process is carried on with a partial loss of fixed carbon due to combustion in the ovens and with complete loss of by-products.

In the by-product type of oven the process of coking is merely one of distillation, with complete recovery of by-products and without any accompanying reduction in fuel value, as combustion does not take place in a by-product coke oven.

Inasmuch as the coke produced from the manufacture of gas in any modern gas retort is not generally suitable for metallurgical purposes, this type will be excluded for the present.

The average yield of coke in beehive practice is approximately 65 per cent. The average yield in by-product practice is approximately $75\frac{1}{2}$ per cent. This difference is accentuated by the enormous production of the Gary and Joliet by-product plants of the Steel Corporation, due to the high fixed carbon content of the mixtures used at these plants. Nevertheless, the normal yield obtained in by-product coke ovens represents a tremendous saving during the course of a year's operation. You are referred to an article fully illustrating this, in the United States Geological Survey paper on "The Manufacture of Coke in 1912," by Edward W. Parker.

The by-product coke industry is directly allied to two important industries: (1) The manufacture of pig iron; and (2) the manufacture of illuminating gas. A further field is its universal use as a fuel to replace crude coal.

PRODUCTION OF PIG IRON.

The following table shows the increase in the production of pig iron in the United States as compiled from the records of the American Iron and Steel Association, from 1890 to 1912, inclusive:

Year.	Gross tons.	Year.	Gross tons.
1890.....	9,207,703	1901.....	15,878,351
1891.....	9,279,870	1902.....	17,821,307
1892.....	9,157,000	1903.....	18,009,252
1893.....	7,124,502	1904.....	16,497,033

*Paper presented before the Western Society of Engineers and printed in the journal of the society.

Reference: Technical paper 50, Metallurgical Coke, by A. W. Belden, Bureau of Mines, U. S. Department of the Interior, Washington, D. C., 1913.

1894.....	6,657,388	1905.....	22,992,380
1895.....	9,446,308	1906.....	25,397,101
1896.....	8,623,127	1907.....	25,781,361
1897.....	9,652,680	1908.....	15,936,018
1898.....	11,773,934	1909.....	25,795,471
1899.....	13,620,703	1910.....	27,393,567
1900.....	13,789,242	1911.....	23,649,344
		1912.....	30,000,000

It will be seen from the above table that the increase in production of pig iron for the past 20 years has been 225 per cent—a production greater than that of Germany and England combined.

ANNUAL ADDED CAPACITY 1905-1912.

Year.	Capacity.
1905.....	1,292,000
1906.....	1,135,000
1907.....	2,065,000
1908.....	1,185,000
1909.....	1,930,000
1910.....	1,794,000
1911.....	565,000
1912.....	1,000,000

This is enough to illustrate the importance of the pig iron industry and its possible growth.

PRODUCTION OF COKE.

Year.	By-product coke.	Beehive coke.	Total.
1893.....	12,850	9,464,730	9,477,580
1901.....	1,179,900	20,615,983	21,795,883
1907.....	5,607,899	35,171,665	40,779,564
1908.....	4,201,226	21,832,292	26,033,518
1909.....	6,254,644	33,060,421	39,315,065
1910.....	7,138,734	34,570,076	41,708,810
1911.....	7,847,845	27,703,644	35,551,489
1912.....	11,048,489	32,868,345	43,916,834

It will be seen from the above that we are at the present time manufacturing only about 25 per cent of the total coke produced in the United States in by-product coke ovens. It is unnecessary to dwell on the wastefulness of the beehive oven; it has been completely replaced in Europe with by-product ovens, and it is only a question of time until it will be completely replaced in this country. It is not now considered in installations for the production of coke, except in localities where it is advisable and almost economically necessary to continue beehive practice. The future field for the by-product coke oven industry in this particular is assured.

Reference to the above table will show that during 1912 there were practically 44,000,000 tons of coke made in the United States, of which amount approximately 11,000,000 tons were made in by-product coke ovens. Assuming an average beehive recovery of 65 per cent, there were approximately 34,000,000 tons of coal converted into coke without the recovery of by-products, and practically the entire amount was consumed in the manufacture of pig iron.

On a conservative estimate, it is safe to say that the loss of these recoverable by-products amounted in value to a sum equalling the total coal that went into the production of the entire 44,000,000 tons of coke.

By-product coke when properly made is equal in quality to the best grade of beehive coke.

By-Product Coke in Its Relation to the Blast Furnace.—There is one disadvantage in connection with the by-product coke oven. It is a fact that many available coals for making excellent coke in Beehive ovens

are not suitable for use in the by-product oven, as the coke so made, while satisfactory chemically and physically, breaks up into pieces too small for use in the blast furnace. There is no question but that this coke could be used for domestic purposes, but unfortunately this is an undeveloped market and will be discussed later. It is also a fact that many coals available for use in the by-product oven and making excellent metallurgical coke cannot be used in the Beehive oven. Therefore, we are forced to admit that both types of ovens are restricted to certain grades of coal. In order to remove the objection to the by-product oven, we have merely to remove the objection to the size of the product from certain coals. This can be done in two ways: First, we must learn to coke these coals in such a way that the objection to size can be removed; second, we must ask the blast furnace men to learn to use the small coke. If the coke produced is satisfactory in all other respects, it should not be rejected on account of size, provided that the size of the coke is suitable to permit its use at the tuyeres of the furnace.

Requirements of Blast Furnace Coke.—Practically all pig iron in this country is made with coke; yet there does not appear to exist any definite standard specifications for the purchase of blast furnace coke. Common practice and usage accepts a coke as satisfactory that possess the following essentials or characteristics:

1. *Chemical Composition:*

(a) An ash content of 10 per cent or under: in other words, the maximum percentage of fixed carbon with corresponding high fuel value. This does not mean that coke containing a higher percentage of ash is in all cases rejected, but beyond 10 per cent it adds considerably to the cost of producing pig iron and is therefore undesirable.

(b) A sulphur content of 1 per cent or less.

(c) A phosphorous content low enough so that the pig iron will not be unduly affected.

2. *Physical Characteristics:*

Under this heading is placed the cellular structure and arrangement, on which depends its compressive and abrasive resistance to the burden in the furnace. Cellular displacement or porosity determines the extent of the spherical area exposed to the action of the blast and rapidity of heat development. The average blast furnace coke has a porosity of from 47 per cent to 50 per cent.

The prime function of blast furnace fuel is to furnish heat. Therefore the higher the percentage of available carbon the fuel contains, the greater its value.

The necessity for low sulphur and ash content is explained by the fact that its removal by fluxing requires added material and heat, the heat being furnished by the carbon in the coke; the added material will be, roughly, twice the weight of limestone per unit weight of ash, and from three to three-and-a-

half times the weight of limestone for every unit weight of sulphur. It is generally estimated that about 25 per cent of its own weight in carbon is required to melt the slag.

These are approximate figures and are given simply to show how the purity of the fuel influences the capacity and quality of production of the blast furnace. As indicated above, one of the most important factors determining the value of fuel is its size.

It is generally conceded among blast furnace operators that the coke in its descent through the blast furnace is only slightly dissolved by the ascending CO_2 , and reaches the level of the tuyeres practically in its original form; it is then reduced to CO . Just what precise size the coke should be at this point, I have never been able to find out, but the furnace men in general agree that the more uniform the coke at this point, the faster and easier the furnace works. This being the case, it should not be difficult to definitely state, providing the coke is properly coked, what the size of the coke should be when charged into the furnace. If this could be determined and definitely specified, many available coals that make excellent coke would be thrown upon the market to be used immediately in the manufacture of by-product coke, and the economic gain to the user would be very great.

AVAILABLE COKING COALS.

It seems that there are two essentials lacking in the necessary combination to enlarge the field of available coking coals: First, specific knowledge of the actual phenomena of coking; second, precise and definite knowledge in the art of its use in the manufacture of pig iron.

1. *Specific Knowledge of the Actual Phenomena of Coking.*—There has been a great deal of technical data published during recent years relative to the behavior of coals under heat. A serious effort has been made to find out why one coal will coke while another will not. The results of these investigations to my mind prove conclusively that the coking quality of the coal depends on the amount and character of certain of the heavier tarry compounds, particularly those of a resinous character. This would indicate at first glance that a coal containing the largest percentage of tar would be the best coking coal. With our present knowledge of coking, however, we know that this is not the case. It might indicate that the heat condition under which the coal is coked is the most important thing in the entire phenomena of coking, and it may be that with certain coals we will have to work with higher temperatures than those which we are accustomed to at present. There is no question in my mind that this is the crux of the whole thing, and is it not important enough to follow along big, practical lines for its commercial importance? Laboratory investigations are futile. Single oven tests do not mean anything. I have in mind a detached block of ovens equipped with recovery apparatus and operated as an experiment station. The coke, gas, and by-products could be util-

ized commercially precisely as the product of the plant proper. The advantage of having this plan as an adjunct to a going concern is that it would be absolutely uninfluenced by any conditions other than those created by the actual carbonization of the coal itself. It would depend for its gas on the main plant, and wherever there is a large available surplus, this would positively insure a constant uniform supply of gas to the ovens. It could be connected to an auxiliary power plant where the danger of fluctuation due to shut-downs would be eliminated. In other words, it could operate continuously under known established conditions which would be constantly identical. The same coal would be used with every possible combination of conditions until actual authentic data were established, prescribing with positive exactness the conditions under which that coal should be coked to produce the most desirable results. These tests could be continued indefinitely with very little cost to a plant already in operation. The tests would not be indicative but a standard of what a plant built along the same lines would produce.

I venture to say that in the course of a few years information of positive and incalculable value will be established. The most important essential in the whole thing is patience and surely the object is worth the price.

2. Precise and Definite Knowledge in the Use of Coke in the Blast Furnace.—With reference to the lack of precise and definite knowledge in the use of coke in the blast furnace, I can imagine the effect that this statement will produce on the average blast furnace man, and am very glad this statement is being made to a somewhat friendly audience. Nevertheless, such a statement must be conceded a fact. The reason is very clear. Up to 1907 or 1908, the standard fuel for the entire country was Connellsville Beehive coke. You are all familiar with the loaflike structure of this coke, and its size was considered one of its strongest virtues. The blast furnace man did not have to bother about his fuel, and his researches did not go beyond what the local condition from day to day necessitated. As recently as 1907 and 1908 it was considered impossible to operate with by-product coke and get the same results as with Connellsville coke. I think the principal objection was on account of its color and size. When we started the Joliet coke plant in 1907 we were visited by coke and blast furnace experts and they were all unanimous in stating that the coke was much too small. We broke it up into too small pieces and the results obtained from the use of that coke at Joliet, South Chicago and Gary have demonstrated how much they were mistaken.

The spherical diameter of the entire coke production at Joliet would not average 4 in. About 40 per cent of the coke will stay on a 2½-in. screen; 40 per cent to 44 per cent will go through a 2½-in. screen staying on a 1⅞-in. screen and the balance will go through the 1⅞-in. screen. The results obtained at

Joliet encouraged the management of a certain blast furnace plant to experiment with crushed coke. Every pound of coke used at their blast furnace goes through a 3½-in. roll crusher, producing the following sizes, which are the averages for 1912:

On 2-in. screen, 75 per cent.

On 1½-in. screen, 17 per cent.

On 1-in. screen, 6 per cent.

On ¾-in. screen, 1 per cent.

Through ¼-in. screen, 1 per cent.

The coke is produced from a mixture of 70 per cent high volatile coal and 30 per cent Pocahontas, making an average volatile matter in the mixture of 29 per cent to 30 per cent. With this mixture and this size coke, a decided improvement was obtained in the furnace and they now have a coke consumption of about 2,300 lbs. on a 53 per cent yield, using a large percentage of briquetted ore. Other furnaces are contemplating the same step.

It will be only a question of time until this problem of size is solved satisfactorily, but would it not be better if every blast furnace man in the country would turn his attention to this problem and thereby hasten its solution? The economic advantages to be gained from such a solution are tremendous, and would certainly mean, in many instances, the installation of by-product coke oven plants, cheaper coke, and cheaper pig iron.

Referring again to the coke-oven operation, I cannot but take time to express a desire that less time and money be spent on the technical side of the industry and a little more on the commercial side. By all means, strive to obtain the greatest possible recovery of by-products, but do not overlook the fact that the revenues to be gained from this source in the future are now slight compared to the returns that could be obtained in finding out the character of certain coals and the method of successfully coking these coals that we are at present rejecting. This is a problem absolutely up to the coke-oven operators. The fact that with the enormous production of coke and the widely scattered localities of the blast furnace, our lack of knowledge on this great economic question practically restricts us to the use of a mixture of two certain coals, is deplored.

Summed up, the by-product coke oven is so close in its relationship to the blast furnace that it is difficult to determine where the relationship begins and ends. It is without doubt an auxiliary to the blast furnace and should be operated for the particular blast furnace where its product is to be consumed. There is no question as to the quality of the fuel produced in by-product ovens, and the fuel is today accepted everywhere. In Germany there is not a pound of fuel used that is not manufactured in by-product coke ovens. England is rapidly getting into the same position. Japan has two by-product coke plants in operation and several others under contemplation. The same can be said of China. It is possible that in the near future

we will be in the position of shipping pig iron manufactured from coke made in American by-product coke ovens to the Pacific Coast.

Another important point should be mentioned before closing this particular subject. The Panama Canal will throw open to us the Pacific markets and a great export trade. There is magnificent ore in Texas of the finest possible quality and in unlimited quantity. There is also excellent coal in the South, but, as is true of the coal in the North, certain grades are considered better for coking purposes than others. In other words, wherever pig iron is manufactured, there will be eventually, by-product coke ovens, and its development is restricted only by the extent of the manufacture of pig iron.

THE BY-PRODUCT COKE OVEN IN THE MANUFACTURE OF GAS.

It has been stated that the by-product coke oven is not so well adapted to the manufacture of illuminating gas as so-called gas retorts. This is not a fact. Continental practice has demonstrated without any question that as regards volume and character of product, the by-product coke oven is just as well adapted to the manufacture of illuminating gas as any gas retort, whether it be vertical, inclined or through horizontals. The unfortunate part of it is that we are up against the same proposition as the gas maker would be if he had no water gas plant. It is impossible to evolve a gas from a coal that will meet with the present universal municipal requirements in practically every state of the Union. I refer to the candle power, which is antiquated and altogether unnecessary.

The modern incandescent mantle depends for its illumination upon temperature only, and if the gas contains the necessary heat value to give the maximum luminosity on combustion, the candle power has no bearing whatever on its value. Mantles are becoming cheaper and their universal use is surely in sight. It is true that the constituents of coal gas, that is to say, those vapors on which the gas mainly depends for its illuminating value, have a large thermal value, but such constituents are only a small percentage of the entire gas volume—not more than 3 per cent or 4 per cent—and they can be recovered from the gas as a marketable product without reducing the heat value of the gas more than 5 per cent. I refer to the extraction of benzol. When a gas is debenzolized, it is absolutely free from naphthalene, a tremendous advantage in its distribution and transmission, and is adequate in every sense for the purpose of illumination in conjunction with mantles.

In regard to the use of gas for domestic and commercial purposes, it is needless to dwell on that phase of the question. Candle power is not a factor. It is plain, therefore, that gas should be sold in the United States on a heat basis, the same as in all other civilized countries. Gas that contains from 550 to 600 B. t. u.'s is adequate for any purpose for which it can be used.

Wisconsin has the following municipal requirements throughout the state:

No candle power; the gas must have a total heating value of 600 B. t. u. per cu. ft. when referred to 30 in. pressure and 60 deg. F. The minimum shall never fall below 550 B. t. u. The sooner every other state in the Union follows this precedent, the better it will be for the gas industry and all parties concerned. The consumer has some rights in this matter, and if a gas can be produced cheaper by the elimination of unnecessary and foolish restrictions, it is only right and proper that the conditions should be met. In eliminating the candle power bogie, the adaptability of coke ovens will become so apparent that their use will be universal.

With the ever-increasing price of crude oil and the ever-increasing demand for a lower-priced gas, there can be but one answer—a cheaper form of production.

One of the latest questions to be raised against the use of by-product coke ovens by commercially-interested parties, is that the manufacture of illuminating gas from by-product coke ovens will in a comparatively few years seriously affect the by-product market and the coke market. Nothing could be more incorrect. The substitution of by-product coke ovens for gas retorts would increase the ammonia yield to some extent, and decrease the tar production. In other words, the effect on the yield of by-products would not be sufficiently great to interfere with the steadily increasing demand for these products, and would not affect their price one iota.

With regard to the effect on the coke market, there is at present about 200,000,000,000 cu. ft. of illuminating gas manufactured in the United States per annum, at least that amount of gas is sold for illuminating or other domestic purposes; it makes no difference what it is used for; that is the amount of gas that is being manufactured. Now, if every cubic foot of this gas was manufactured in by-product coke ovens on coals averaging 10,000 cu. ft. of gas per ton (provided the ovens were operated on producer gas, previously cleaned, and from which the ammonia had been recovered and this gas regenerated), the amount of coke thrown on the market from such a production would not amount to 50 per cent of the coke consumed in the production of pig iron alone. Not only this, but the greatest field for the use of coke has not yet been touched.

I think we can, therefore, dismiss any statement that deprecates the adaptability of the by-product coke oven to the manufacture of illuminating gas or, as a matter of fact, to the production of gas used for any purpose whatsoever.

Recovery of Benzol.—Before leaving this subject, I will refer again to the recovery of benzol. This is an enormous industry in Europe. There is not a motor car in Paris or Berlin that does not use benzol for power. Today practically the entire amount of it re-

covered in the United States is used for enriching illuminating gas. Remove the candle power factor and this benzol will be thrown upon the market. We all know that the price of gasoline is increasing, and every man who runs an automobile or an auto-truck will welcome any fuel that is equally as satisfactory, at a slightly reduced price. There is a demand for such a commodity and we have no supply. Benzol is 10 per cent to 15 per cent higher in efficiency than gasoline, and, contrary to popular opinion, it can be burned in any carburettor that will consume gasoline.

The average coking coal yields from $1\frac{1}{2}$ to 2 gallons of benzol per ton of coal carbonized. Placing a value of 10c per gallon on this, it is unnecessary to go further into the advantages to be gained from the recovery of this product.

RELATION OF BY-PRODUCT COKE OVEN TO THE COAL INDUSTRY.

The coal production in the United States for 1912 amounted to 500,000,000 tons. Its estimated value was approximately \$700,000,000, the record so far for any single year, and it was about one-half of the world's production. The growth of the industry is shown below:

In 1850	11 states produced	7,018,181 short tons.
In 1860	15 states produced	14,619,042 short tons.
In 1870	21 states produced	33,035,580 short tons.
In 1880	25 states produced	71,481,570 short tons.
In 1890	28 states produced	157,770,963 short tons.
In 1900	28 states produced	269,684,027 short tons.
In 1910	27 states produced	492,647,863 short tons.
In 1912	28 states produced	511,964,403 short tons.

The output has doubled every ten years. The production of coke in 1912 amounted to 43,000,000 tons only and was, as shown practically all consumed for metallurgical purposes.

In a comparatively few years the combustion of soft coal will not be permitted in the big centers. How would such an ordinance affect New York and Chicago as an example?

No definite statistics are available for New York, but it is conservative estimated that the amount handled is 32,000,000 tons per year. Because of the smoke restrictions in effect, the consumption of soft coal is less than 5,000,000 tons per year. It is estimated that over 12,000,000 tons of anthracite are consumed in New York proper.

Chicago handles over 21,000,000 tons of coal per year, principally soft coal.

The state of Illinois produced over 50,000,000 tons of coal in 1912.

The railroads consume, within the city limits, over 5,000,000 tons of coal per year.

These conditions apply to other big centers in proportion.

It is easy to imagine the replacement of soft coal in these centers, and they would support several plants the size of that at Gary in any one locality. When consumers learn that coke is not only the clean-

est possible kind of fuel but the cheapest, its use will be universal.

Furthermore, all students of economy are unanimous in stating that the use of coal in crude form for any purpose whatsoever is an economic crime. There is no purpose for which coal is used today but what the same amount of work can be performed with the same cost or less with coke. Political economy teaches that there is no source of real wealth other than land and labor and one of the most priceless possessions we have is our coal supply. If you consider an average value of 50c for the by-product that can be recovered from a ton of the average coal, there is \$250,000,000 in pure wealth destroyed annually at our present rate of consumption.

To sum up, there is no doubt that natural development will take care of the present reckless extravagance in the use of our raw material. It is also perfectly obvious that this will have to be followed along sane and reasonable lines, but without any unnecessary lapse of time. Statistics have shown that 75 per cent of the total coke produced is made in ovens of the non-recovery type. These plants represent a vast amount of capital, and the present locations of the blast furnaces are such that it is questionable, even when taking into consideration the tremendous saving to be obtained from the modern process of coking, whether such plants could be commercially profitable in certain localities.

About 40 per cent of the total freight revenues of the railroads is derived from the transportation of coal and coke. This freight tariff plays an important part in the location of a by-product coke plant. In other words, every locality has its average price for coke and this price will vary as the distance from the source of supply. It is, therefore, obvious that if no coals are available other than those at present supplied for use in the production of coke, the situation becomes one of purely commercial reasoning, whether the amount of money saved in the price of coke per ton would pay for the investment required. But suppose there are coal fields available with a considerably reduced freight rate; the question then is not one of returns on the investment, but on how fast the plant can be built, because the coke could be produced at a price that would absolutely exclude any product that had a less favorable freight rate.

The smallest unit of by-product coke oven that can be constructed with any degree of commercial success will cost, roughly, \$1,000,000, hence it is obvious that the proposition must be studied very carefully from all angles and reduced to its final terms; its installation will depend entirely on its location.

With reference to the relationship of the market for by-products to the coke industry, I am informed that a market is absolutely assured as long as the industry develops in a sane and reasonable way. I have been furnished with data and pictures from the Ameri-

can Coal Products Company which will illustrate the enormous advantage to be gained by the farmers from the use of ammonium sulphate, and I desire to express my thanks to that company for their courtesy and interest in this matter.

You are referred to a paper which was read by Mr. W. N. McIlravy before the American Gas Institute in 1911. It describes the status of the by-product industry to date.

I feel sure that we can depend upon natural conditions, natural growth, and natural conservatism to create the demand for by-product coke ovens. In order to place the industry in its proper position, it is necessary to educate those who are not familiar with the subject: to give them plain, simple facts. Unfortunately the business in the past has been shrouded in mystery and a mass of technicalities. It is not a simple art. It is a fact that intelligent skilled labor and well-trained minds are required to properly and successfully carry out the policy of a coke plant and develop it to its utmost capacity. But the bulk of the actual work is performed by common labor and there is nothing about it that is in any way more complicated than the operation of a modern blast furnace or an open hearth steel plant. The success of the plant, of course, depends on experience. The plant policies must be carried out by men trained for the purpose, and it takes a long time to acquire the necessary experience to formulate and to carry out these policies, but we have enough material in the country to draw from. Our universities are sending out such men, and after a certain amount of training at a small expenditure of capital, they develop into suitable material for whatever needs may arise. The field of by-product coke manufacture is one of the most promising industries, and I would like to urge upon those directly or indirectly interested, to encourage men of the right kind to enter that field.

OPERATION OF A MODERN COKE PLANT.

Following is a description of the operation of one of the most modern coke plants in the world. This plant carbonizes about 10,000 tons of coal per day. The entire amount of coke produced is used in the manufacture of pig iron. The surplus gas produced is consumed in the different parts of the adjacent steel mill.

The coal mixture used at this plant is 80 per cent Pocahontas and 20 per cent high volatile from the Pittsburgh district. The coal is brought by rail into the plant and unloaded into receiving track hoppers. From there it is conveyed by belt conveyors to the coal crushing building. Here the coal is first passed through Bradford breakers, where the impurities such as slate or pieces of wood, draw-bars or coupling pins, in fact refuse of any character, are ejected from the breakers; the good coal is broken and passed through the openings in the screens.

A Bradford breaker is simply a cylindrical screen

with holes of suitable diameter, usually about $1\frac{1}{2}$ -in. to 2 in. It is equipped with shelves which carry the coal in the direction of the travel of the machine. When it reaches the top it drops on a plate. Naturally anything soft enough to break into a size sufficiently small will pass through the openings so that the slate is not entirely ejected. It is a very efficient method of separating foreign matter from the coal.

After the coal has passed the Bradford breakers, it is conveyed to the pulverizers. Before entering the pulverizers it passes over a suitable apparatus designated as a magnetic separator, where the smaller pieces of iron are removed. This apparatus consists usually of a magnetized pulley over which the conveyor belt travels, or a magnetized plate over which the coal is allowed to slide. The plate being centrally pivoted it can be swung out at stated intervals and the scrap iron recovered.

There are several kinds of pulverizing machines. They are all operated on the same principle. One of the most efficient is the so-called Hammer Mill, which consists of a series of hammers supported by suspension bars. The shaft operating these hammers is directly connected to a suitable sized motor and travels at the rate of 500 to 600 r. p. m., a very rapid rate. The coal is fed in comparatively thin layers over an adjustable screen with perforations of the desired degree of fineness. The impact of the hammers on this layer of coal pulverizes and forces the coal through the screen. The plant described crushes the coal to a fineness of about 85 per cent through a $\frac{1}{8}$ -in. mesh. Coals have varying degrees of hardness and it is necessary to make separate adjustments for each kind of coal. Therefore the apparatus necessary for the preparation of coal is divided to avoid continuous adjustments.

After the coal has been pulverized it is conveyed to a mixing bin. This bin is a double compartment from where the coal is fed onto separate conveying belts and conveyed to a point immediately over the mixers, where the coal is mixed in the different proportions desired. Since both of the conveyor belts to the mixing machine are traveling at the same rate of speed, having the same carrying capacity per unit of time, it is simply a question of adjusting the depth of feed on the belt in order to arrive at a reasonable degree of accuracy in the ultimate mixture.

From the mixing bin the coal is conveyed to the storage bins at the battery. The storage bins are usually so constructed that they have a 24-hour supply for the entire plant. It is customary to do all the crushing by day so that proper inspection and repairs may be made on the coal-handling equipment by night. As a modern coke plant operates continuously 24 hours per day, this question of coal supply is a very important one.

From the coal storage bins at the ovens the coal is charged into larry cars, which operate on tracks ex-

tending the entire length of the battery. It is unnecessary to say that they are operated electrically, as every part of the apparatus of the plant is so operated wherever possible.

The coal is discharged from the larry cars into the ovens, where it is leveled to permit of a free path of travel for the gas evolved during the process of coking. From the time the oven is sealed, the charge remains undisturbed until it is ready to push out.

The process of coking consists merely in driving off the volatile matter in the coal by means of heat radiation from the heated oven walls. It is purely a process of distillation. Therefore, coke is the solid residuum and consists of approximately 90 per cent carbon, the balance being the ash with such impurities as sulphur and phosphorus. The amount of ash and other im-

breeze, usually about 3%. Everything that goes over $\frac{3}{4}$ in. is considered suitable for the blast furnaces. There is also an appreciable increase in yield of combustible matter due to the breaking up of the tar vapors in the passage of the combustible matter through the heated mass of coke. But practically speaking, the fuel value of the coke is in direct proportion to the fuel value of the coal entering into its production.

We will now follow the gas as it is evolved from the coal. As previously stated, the coal is leveled to allow the gas a free path to the offtake pipe, which is situated at the end of the oven. The gas ascends this offtake pipe into a so-called collecting main and from there travels by means of mains to the condensing house. The gases leaving the oven chamber are about

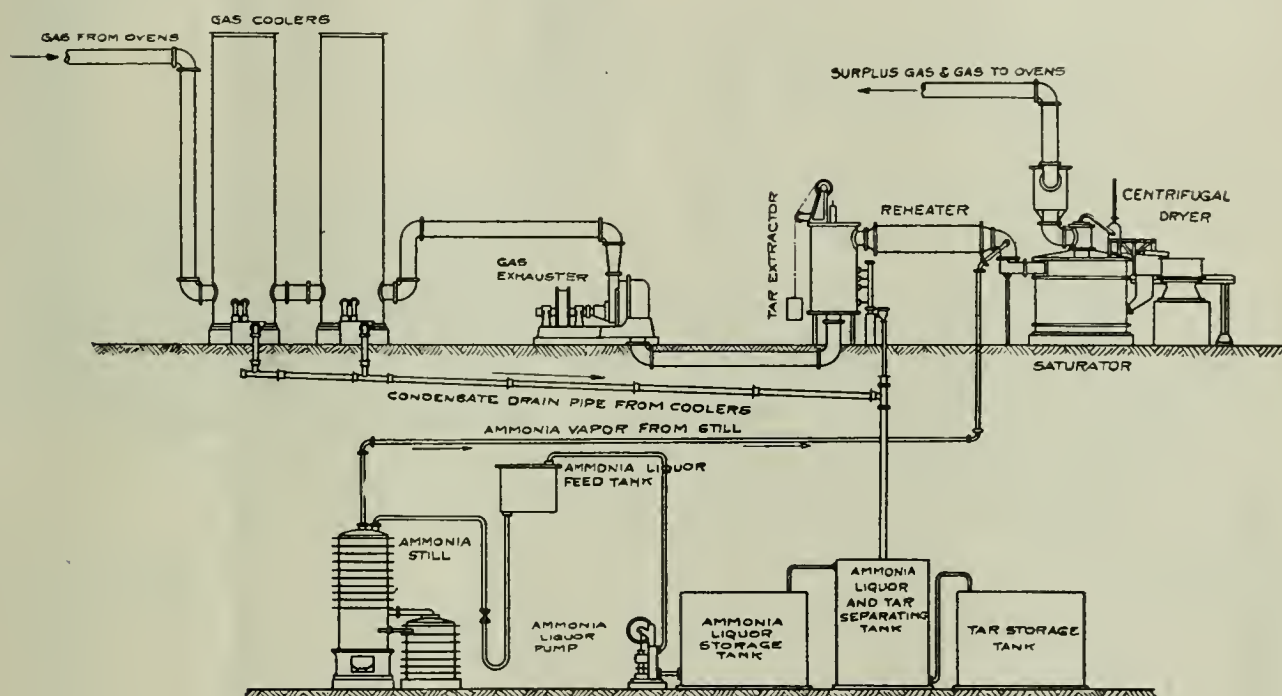


Fig. 1—Process for Direct Recovery of Ammonium Sulphate—Koppers Patent.

purities in the coke depends entirely on the amount in the coal used, as these substances remain in the residue from distillation. It is scarcely possible to eliminate all of the volatile matter, and usually 1% to 1½% remains, which is in the form of heavy tarry compounds of a fatty character, not easily driven off. When the volatile matter has been practically eliminated, which is usually accomplished in from 16 to 18 hours, the oven is ready to push. The doors are removed and an electrically operated pusher machine takes its place in front of the oven; the ram is carefully set in position against the face of the coke mass and propelled through the oven. The coke is discharged through the other end of the oven into a receiving car, which conveys the coke to the quenching station, where the coke is quenched by means of water. The coke is then screened; the object of screening being to free the coke from the fine dust or

1,000° F., and this temperature is gradually reduced to about 200°. The reduction in temperature precipitates the bulk of the condensate from the gases. This condensate consists of tar, oils, and the moisture originally in the coal and the amount formed during the process of coking, and drains into settling pans or tanks, where, owing to the difference in specific gravities, the separation is easily carried out. The water is slightly impregnated with ammonia and is usually known as weak liquor to differentiate it from the strong ammonia liquor which is produced in another phase of the operation. The tar, after undergoing a period of decantation, is shipped in tank cars.

We will now follow the gas which passes through the by-product recovery house. Fig. 1 illustrates the various steps described below. The gas still contains traces of tar and water vapor, and in order to remove these elements the gas is passed through the primary

coolers. The coolers are rectangular in shape and consist of a series of standard steel boiler tubes through which water is constantly flowing and around which the gas traverses. The whole operation is on the counter-current principle. The gas then enters the exhausters. These can be of either the positive displacement type electrically-operated or the modern turbo type. Up to this point the gas has been under suction, the amount of suction depending on the distance the gas is drawn from the ovens. The controlling factor in the operation of the exhauster is the pressure desired at the ovens. It is usually considered good practice to operate as nearly as possible to zero within the oven chamber, or at any rate not more than $\frac{1}{2}$ mm. to 1 mm. back pressure.

From the exhausters the gas under pressure is forced through tar extractors to remove the final traces of tar. The tar extractor is a very ingenious piece of apparatus, consisting of a so-called basket made up of sections of thin plates perforated and set up in such a way that the perforations are staggered. After the gas has been forced through the perforations it is usually quite free from tar. The principle is very simple. As the gas is forced through a perforation it impinges on the solid section of the plate ahead so that any liquid globules are arrested, broken up, and trickle down the surface of the plate. The gas after passing through the basket is forced through the reheater, which is similar in design and principle to the coolers, but, instead of water passing through the tubes, live steam is used. The gas, after being reheated to a temperature of 50°C ., passes into the saturators, containing a saturated solution of ammonium sulphate and about 5% of sulphuric acid. The reaction and precipitation is almost instantaneous. The salt is ejected and allowed to drain; then it is centrifuged and conveyed into the storage house, where it is ready for shipment—usually in sacks of 200 lbs. bulk. The sulphate received from this process is perfectly white and contains at least 25% of ammonia and only 0.1% to 0.2% of sulphuric acid. The weak liquor previously mentioned is distilled and the ammonia vapor is directed to the header in front of the saturators where it mingles with the gas. In this way the entire recovery is complete.

This process has many advantages, among which are:

1. Extreme simplicity.
2. Small amount of space required.
3. Ammonia washers unnecessary.
4. Less pumping capacity required.
5. Less steam consumption.
6. A higher degree of ammonia recovery.
7. Can be installed in any climate because independent of temperatures of water supply.

We have now covered the coke, tar and ammonia. It remains to briefly mention the gas.

By-product coke oven gas has an average heating value of from 450 to 600 B.t.u. per cu. ft. This is a

wide latitude, but the character of coals we have to deal with and the different purposes for which the gas is used allow the production of gas within the range of these figures. The average coking coal will produce about 10,000 to 11,000 cu. ft. of gas per ton of coal. About 50% of this is required for combustion at the ovens to carry out the coking process. The balance is considered surplus gas, and can be used either for illuminating purposes or for replacing other forms of fuel. One of its principal uses in steel mills is the

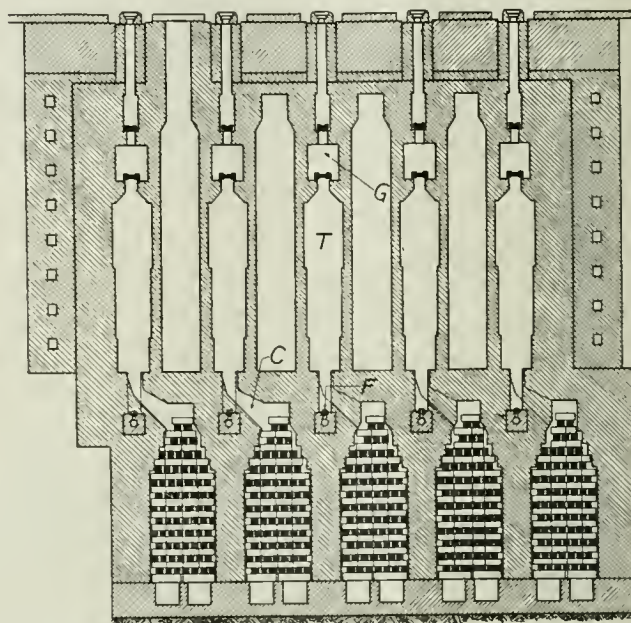


Fig. 2—Cross Section of Regenerator and Ovens.

replacement of coal under boilers for the generation of steam power. In Germany it is used extensively in open-hearth furnaces and this practice is in evidence in this country to a small extent. In Germany it is considered the best kind of fuel for open-hearth furnaces, on account of the higher temperatures obtainable, better economy, both in the use of heat and in the construction of the furnace, increased tonnage, and lower operating costs as compared with producer gas. The gas was first used in the same manner as producer gas, being regenerated before reaching the combustion chamber. This was found unsatisfactory and is unnecessary as its high heating value enables sufficiently high temperatures to be maintained without regeneration. It was proved that the gas lost approximately 9% of its heating value by preheating. This would depend to a very great extent on the character of the gas regenerated.

However, the gas is now used cold and only the air is regenerated, which allows smaller regenerating capacity and cheapens furnace construction. On account of the high heating value of coke-oven gas, a temperature may be maintained considerably higher than with producer gas, allowing a greater tonnage for the furnace. The output in some cases has been known to increase from 15% to 20%.

Some of the objections to the use of by-product coke oven gas in open-hearth furnaces are that it shortens the life of the furnace; and that the gas has a tendency to rise and burn along the roof of the furnace instead of immediately over the metallic bath. These difficulties are merely mechanical and obviously can be overcome. We have information where the roof of a furnace has actually stood more heat than with producer gas, while the life of the checkers was greatly increased. The efficiency in the use of producer gas will increase as the workmen become better acquainted with its different characteristics. Its value as a fuel will depend on the locality and the nature of the fuel it is replacing. Its minimum value is when it replaces coal under boilers; its value increases when used to replace crude oil; and its maximum value is

shows the relative position of the regenerators to the oven chamber and the direct connection of the regenerators to the heating flues.

The hollow walls forming the coking chamber are constructed to form a series of vertical flues opening into one common horizontal flue, extending the entire length of the wall. (See *G*, Fig. 3.) It is in these flues that combustion takes place and the heat transmitted through the material of the walls into the coal mass.

The coking chamber is sealed at either end by heavy iron and steel doors, either of the self-sealing type or of the plug type, resting against the wall jambs and sealed with luting clay. Each door on the pusher side is equipped with a small self-sealing door large enough to permit a traveling bar to enter for the

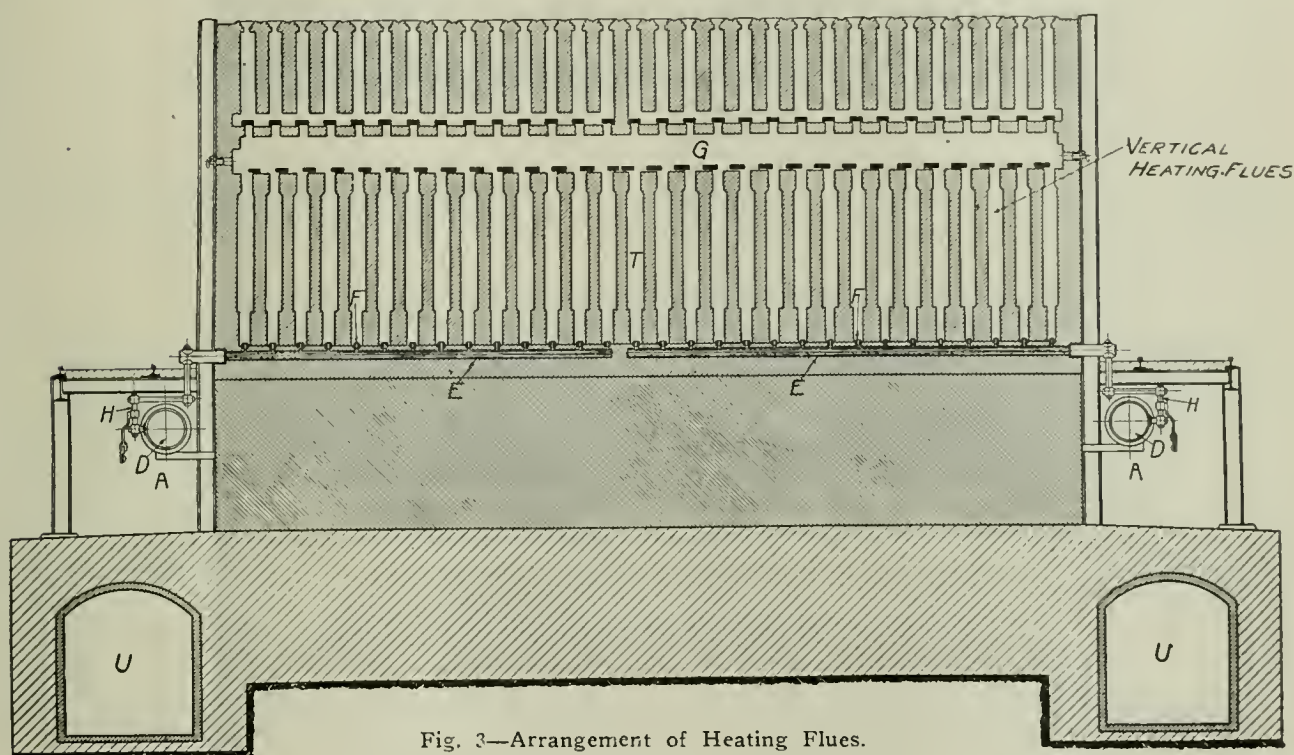


Fig. 3—Arrangement of Heating Flues.

when used for illuminating purposes. In other words, the value of the gas is strictly one of utility and will vary under varying conditions.

The average coking coal will yield from 5 to 7 pounds of ammonia and from 6 to 10 gallons of tar. It is the recovery of these by-products and their steadily increasing value that makes the by-product coke oven possible.

KOPPERS' CROSS REGENERATIVE BY-PRODUCT COKE OVENS.

A battery of Koppers' ovens consists mainly of a series of hollow walls, built of the finest silica material—really silica beams resting on foundations extending to rock or some equally satisfactory bearing material. The space between the walls is divided horizontally into two compartments, the upper forming the coking chamber and the lower the regenerators. Figure 2

purpose of leveling the surface of the coal charge so that the gases evolved during the coking process may have a free and uninterrupted path to the offtake usually located at the end of the oven, and through which they are drawn to the by-product recovery plant.

The coal is charged from larry cars through openings or charging holes in the roof, usually four in number, equipped with self-sealing covers.

Figures 3 and 4 show a longitudinal section of the oven chamber, regenerators, and heating flues, as well as the position of the charging holes and the gas off-takes.

It will be seen from the above that the process of coking in a by-product oven is merely one of distillation carried on in a chamber from which air is excluded.

COURSE OF COMBUSTION.

A line drawn vertically through the center of a longitudinal section of the heating flues and regenerators (Fig. 3), will enable the course of combustion to be easily followed. Combustion takes place in the flues on one side of this line and proceeds upward; the products of combustion travel across the horizontal flue *G*, Fig. 3, and downward through the set of flues on the other side, through the regenerators (Fig. 4) and to the stack. The process is automatically reversed at periodic intervals usually of 30 minutes' duration.

CHARACTER OF GAS REQUIRED FOR HEATING.

The heat required to coke a given unit of coal is generally less than 50% of the total thermal value of

channel *E* (Fig. 3). This channel is located immediately under the vertical flues and extends the entire length of the ovens, being dead-ended in the center. It is formed by a series of bricks of special shape, making an absolutely air-tight duct. At the base of each flue is an opening in which the gas nozzle *F* rests, and through which the gas flows from the gas duct into the flue for combustion.

The air for combustion is drawn into the chamber at the base of the regenerator, ascends through the checker work, and is raised to a temperature probably around 1,800° F. This highly heated air then passes through the ports *C* (Fig. 2) at the base of each flue and mixes with the gas at a point about level with the floor of the oven.

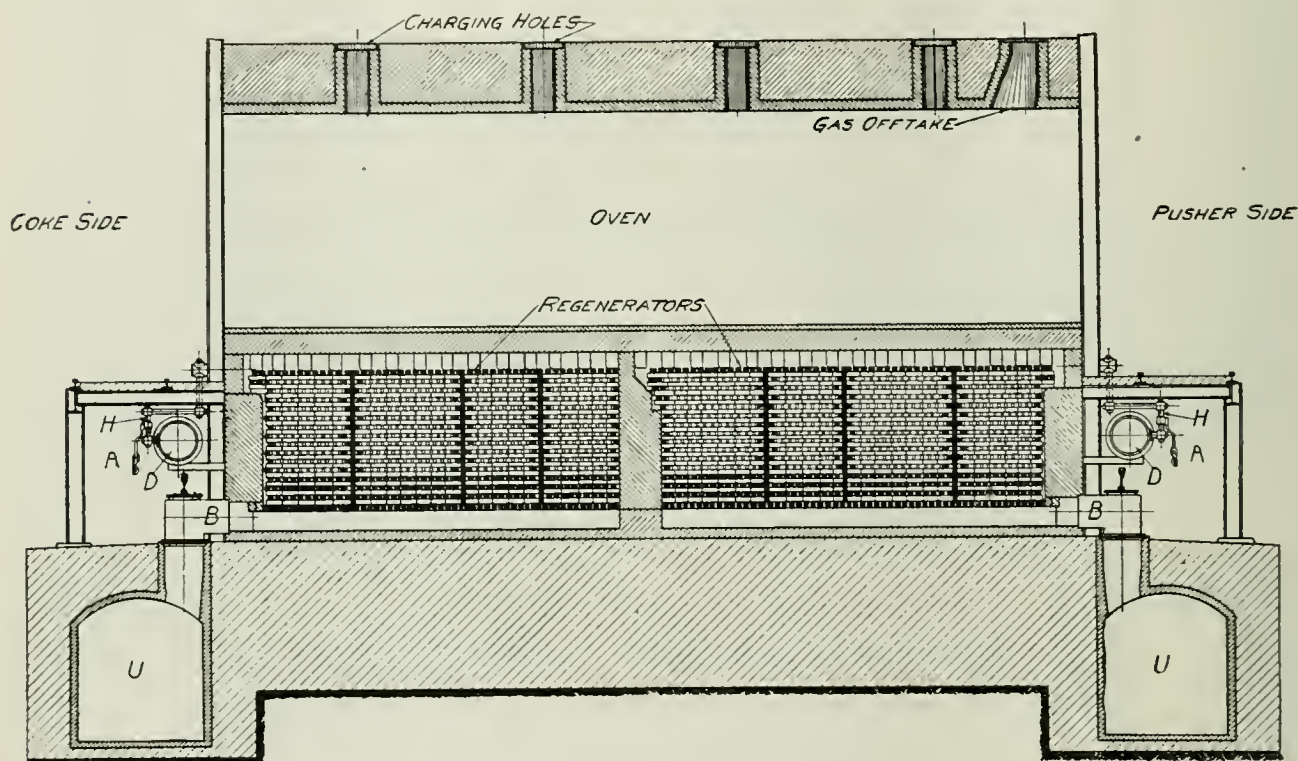


Fig. 4—Longitudinal Section of Oven Chamber and Regenerator.

the gas evolved by its distillation. It is customary to use the required amount of oven gas for this purpose after it has been freed from the by-products. It may be that this gas has such a value that it is desirable to render the entire amount of coal gas available for sale, in which case combustion in the oven flues can be maintained by the use of a cheaper fuel, such as the gas from producers operating on a lower grade of coal; or, as in some cases, blast furnace gas is used.

METHOD OF DISTRIBUTION AND REGULATION OF COMBUSTION.

The manner in which combustion takes place, its distribution and regulation, can be seen by referring to Figs. 2, 3 and 4.

Distribution:

The fuel gas is delivered to the battery in the main *D* (Fig. 4), and ascends the riser pipe *H* into the gas

The burning gases ascend the set of flues on one-half the length of the oven, the products of combustion follow the path of the horizontal flue *G* and pass downward through the vertical flues on the other half, through the ports *C*, Fig. 2, through the checker work into the chamber at the base of the regenerators, and thence by the stack flue *U* to the stack.

It will be seen from the above that each wall is a separate heating unit, having its own gas and air supply. It also has its own regenerator, which is directly connected to the stack and is equipped with a regulating device so that the stack draft can be regulated at will.

It then follows that in order to have the same heating conditions for each oven, all that is necessary is to maintain a uniform supply of gas in the mains *D*

and the same amount of stack pull at the base of each regenerator outlet into the stack flues *U* (Fig. 3).

The individual cross-regenerator permits a much greater capacity than the longitudinal. The Koppers' individual regenerator has a capacity four times greater than that in general use in other types. The protected location of this type of regenerator makes the substructure simple in character, much less liable to expansion defects, and permits of less radiation. The individual regenerator is an essential feature of the Koppers' system.

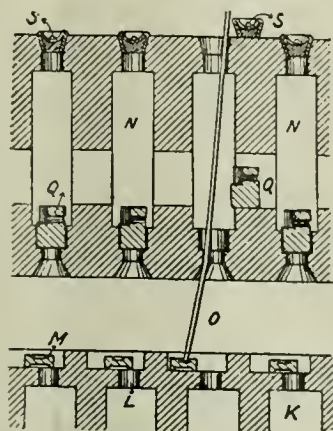


Fig. 5.

Regulation of Combustion:

We have followed the course and distribution of combustion and it remains to show the method of heat regulation. It is this particular feature of the Koppers' ovens on which we desire to lay stress. When an oven is charged, we have a long, narrow, rectangular mass of coal about 35 ft. long, 9 ft. high, and 19 in. in width exposed to the surface of a highly heated wall on both sides. These walls are made up of 30 flues in which continuous combustion is carried on.

The object is primarily to transmit the required amount of heat into the coal so that the entire mass will coke uniformly and in the shortest space of time.

Eliminating all refinements, the chief factors are:

The rate at which coal will absorb heat.

The rate and intensity at which combustion can be maintained.

The amount of heat generated that can be transmitted through the oven wall into the coal.

The product of the above means the shortest possible coking time and maximum tonnage.

Before the above equation can be balanced, we must insure a *uniform transmission* of heat over the entire surface of the coal exposed to the heating action of the walls. In order to do this, we must maintain a uniform intensity of combustion throughout the entire length and height of the heating flues that form the oven walls. To maintain such an ideal condition, we must have control over every square foot of heating surface, and in order to have this control, there must be *accessibility* to every part of the heating system;

not only up to the oven itself, but including the oven proper.

We have shown that the first step necessary is to be assured that each oven has exactly the same capacity for combustion. Each oven must have the same supply of air and gas, and the products of combustion must be drawn away at a uniform rate.

The Koppers' oven generally depends on natural draft for supplying the air for combustion and for drawing away products of combustion. The flue dampers and air valves control the rate at which these functions are performed. It is obvious that up to this point everything is accessible and under positive control.

The regulation of the combustion in the heating flues is carried out in the following manner:

Reference to Fig. 5 will show that there is an opening extending through the roof construction into each flue. In fact, this opening is a continuation of the flue proper, but is closed by means of the cover brick described later. The removal of the cast-iron cover from this opening exposes the entire surface of the exterior of the flue for inspection. In this manner observation of the combustion taking place throughout the entire length of the oven is made easy. The gas opening at the base of each flue is equipped with a nozzle having a definite size opening so that it is possible to increase or diminish the amount of gas admitted to each flue. Alongside this nozzle is the air port. These ports are all calculated for an excess air supply, but they bear an exact relationship to the

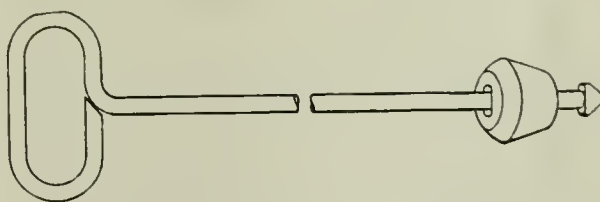


Fig. 6—Gas Nozzle and Rod for Removing It.

area of the vertical flues. It is then only a question of regulating the amount of air drawn into each flue and fitting the opening at the base of the flue into the gas duct with the proper size gas nozzle in order to obtain precise intensity of combustion desired. Reference to Fig. 5 will show how this is accomplished. It will be seen that at the bottom of the horizontal chamber *O* is an opening covered by a sliding brick *M*. This sliding brick is an adjustable damper controlling the amount of draft for each flue.

A little farther up in the chamber will be seen another opening which is completely closed by a cover brick *Q*, except during inspection and regulation. The opening is finally closed on the top of the battery by the lid *S*; by taking off this lid *S* and sliding back the intermediate cover brick *Q*, an unrestricted view is obtained of the interior of the vertical flue. It is a simple matter to adjust the sliding brick damper, *M* to the extent desired in order to obtain any intensity

of combustion. That is the only practical way to decide on the amount of air required for each particular flue. Assuming that a local over-heating occurs in any part of the oven wall, it is simply a question of opening up those particular flues, taking the nozzles

The prime object of a coke plant is to make coke with the recovery of as high a yield of by-products as is consistent with proper operation. In the gas oven the conditions are reversed. The prime object is to produce as high a yield of gas as possible and of the proper quality. It is undesirable to use any of the gas distilled from the coal for fuel. Its value is too high. It is, therefore, desirable to install a producer plant, using a low grade of fuel. The producer gas is cleaned, regenerated, and burned at the ovens to maintain the process of carbonization. It also may be advisable to recover the ammonia from the producer gas and in this way a very low cost fuel can be obtained.

Reference to Fig. 7 will show the changes in construction. The regenerator chambers are subdivided by a partition wall with openings extending into the combustion flues as shown in the coke oven. Air and gas are regenerated in alternate sets of regenerators. For illustration, air would enter the passageway at the base of the regenerators, and the gas would enter the openings in the regenerator chamber. Air and gas follow the same direction, combustion following

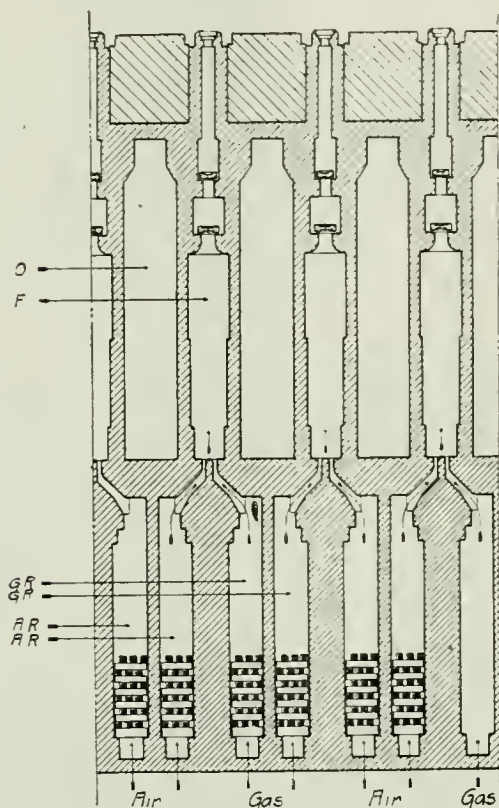


Fig. 7—"B" Koppers Cross Regenerator Gas Oven.

out and putting in a smaller size, or vice versa, by means of the rod shown in Fig. 6. Once a regulation has been made for an entire oven or for any number of ovens, it is not necessary to interfere with the regulation until the general conditions require changing. Once a regulation for any definite coking time is established, it is simply a question of raising or lowering the gas pressure, increasing or diminishing the stack draft. The value of the accessible flue is then not only that of inspection but also of regulation.

If an oven charge is pushed and the coke is not perfectly uniform throughout, it must be evident that to be able to inspect and correct conditions for that particular oven, is a big advantage. The ability to positively control the rate of coking means that the maximum efficiency can be maintained as regards output per battery, and this efficiency can be expressed in dollars and cents.

KOPPERS' REGENERATIVE GAS CHAMBER OVEN.

Reference to Fig. 7 will show that the construction of the gas chamber oven is merely a modification of the regenerative coke oven.

Combustion in coke ovens is usually carried on by utilizing part of the oven gas after being freed from by-products. As stated, this requires about 50% of the total gas evolved.

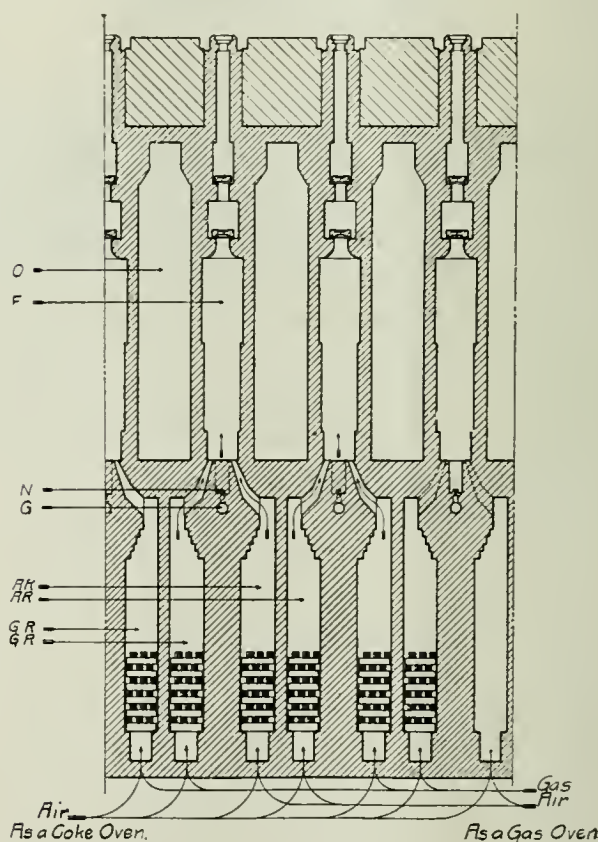


Fig. 8—"C" Koppers Cross Regenerator Gas Oven.

precisely the same course as in the coke oven. The advantage of dividing each regenerator into two sections and passing the same material through each regenerator, whether it be air or gas, lies in the fact that should the division walls develop leaks, no harm can be done as the material is precisely the same in each set of regenerators.

It will be noted that there is no fuel gas duct extending under the flues as in the coke oven. The producer gas is regenerated and enters the vertical flue through the openings or ports leading directly from the regenerator chamber into the flues.

KOPPERS' REGENERATIVE COMBINATION COKE AND GAS OVENS.

The Koppers' regenerative combination oven, Fig. 8, has been designed to act as a coke oven until such time as the demand for gas makes it advisable to operate as a gas oven.

The only difference between this oven and the gas oven is the addition of the gas distributing flue as shown in Fig. 8. This oven can be operated as a coke oven, the regenerators being used in the usual manner exclusively for air. Coal gas should never be regenerated.

When the demand for gas increases, the producer plant is installed and the ovens are then operated as gas ovens, using the producer gas as fuel. It is, of course, necessary that re-adjustment take place for any change in condition; that is to say, though the ovens can be operated as a gas or coke oven alternately, time must be allowed for adjusting to new conditions. It may be advisable, for instance, to operate as a gas oven in the winter and as a coke oven in the summer.

This type of oven is well adapted to localities where the present gas demand is equal to the surplus gas output of the battery and where future indications are that the demand will be doubled.

PHOSPHATE FIELDS OF SOUTH CAROLINA.*

By WM. H. WAGGAMAN.†

The first important discoveries of phosphorites or amorphous phosphates made in this country were those of South Carolina. For many years these fields furnished most of our supply and much of Europe's. But during the last 20 years the output has been gradually diminishing, owing in part to the exhaustion of the more readily accessible rock, but chiefly to the marketing of higher-grade phosphate from other sources.

Although many interesting and valuable articles and papers on these deposits have been published from the time of their first exploration in 1868 down to the year 1904, conditions in these fields have changed so materially during the last decade that it is thought advisable to issue the present bulletin. This reviews briefly the history of South Carolina phosphates, describes the present methods of mining, and handling the rock, shows what disposal is being made of the product, and discusses the future of the industry.

HISTORY.

The existence of the phosphate stratum was known

for many years before its true nature and value were recognized. As far back as 1839 the upper portion of the heavy marl (including the phosphate stratum) was known as the "Fish Bed" of the Charleston Basin on account of the numerous teeth and bones of marine animals contained therein. In 1842 Edmund Ruffin made an agricultural survey of South Carolina, but his report, which was issued the following year, dealt chiefly with the occurrence and extent of the marls of the state. Holmes states that he and some of his associates submitted samples of the nodular phosphate to Ruffin for examination, but apparently no determination other than that of their line content was made. Holmes, in 1844, described "a remarkable bed of nodules or conglomerates 12 inches thick bedded in clay which overlaid the heavy beds of marl."

Tuomey, who succeeded Ruffin, issued a report in 1848 in which he described the same stratum and called the phosphate nodules "marl stones." He was convinced that they were derived from the underlying marls, for he says, "There is little more left than the silica and alumina of the marl." In the appendix of this same report are a number of analyses made by Prof. Charles U. Shepard showing the phosphate content of the marl, but none showing the amount of phosphoric acid in the nodules. Holmes, in a later publication, also regards the phosphate nodules as silicified fragments of the underlying marl.

Chazal states that Prof. Charles U. Shepard was the first to point out the true value of the phosphate nodules. He quotes from a lecture delivered by Shepard before the medical society in 1859, which indicates that the latter was then acquainted with the nature of the phosphate stratum. Chazal also quotes from letters which show that Shepard had advised the use of the Ashley phosphates in lieu of bones as far back as 1860. The outbreak of the Civil War, however, put a stop to fertilizer operations, and it was not until 1867 that Dr. St. Julien Ravel, Dr. F. S. Holmes, and Dr. N. A. Pratt revived interest in these deposits and obtained capital sufficient for their exploitation. To Dr. Pratt belongs the credit of the first recorded analysis of high-grade South Carolina phosphate:

From 1868, when 12,262 tons of rock were produced from the South Carolina fields, to the year 1893, which showed a production of 618,569 tons, the industry steadily grew, but since the latter due the production has diminished, till in 1911 the total amount mined was only 161,156 tons.

GEOGRAPHY AND TOPOGRAPHY.

The phosphate area of South Carolina lies along the coast in a belt, which is in places fully 20 miles wide, extending from the Wando River in Charleston County to the Broad River in Beaufort County (see Fig 1). The coast region as a whole is very little above tide level and is intersected with numerous creeks, rivers, and arms of the sea. Most of these streams are navigable and afford the phosphate operators a ready means of transportation for their product. Many of

*From The American Fertilizer.

†Scientist in Investigation of Fertilizer Resources, U. S. Department of Agriculture, Washington, D. C.

the phosphate properties are reached by the Atlantic Coast Line, the Southern, and the Charleston & Western Carolina Railroads, or spurs from these roads.

CLASSES OF PHOSPHATE.

The South Carolina phosphate deposits are usually classified under two heads, namely, the "River Rock" and the "Land Rock."

The River Rock was at first the most easily exploited, since it was cleaner and after being dredged from the river bed required but little subsequent treatment to make it a marketable product. It was some time before a satisfactory method of mining and cleaning Land Rock was devised. The two types of phosphate, however, are practically identical, the River Rock being merely the Land Rock washed down and concentrated in the river beds.

The mining of river phosphate has now ceased and the rock shipped from South Carolina is all from

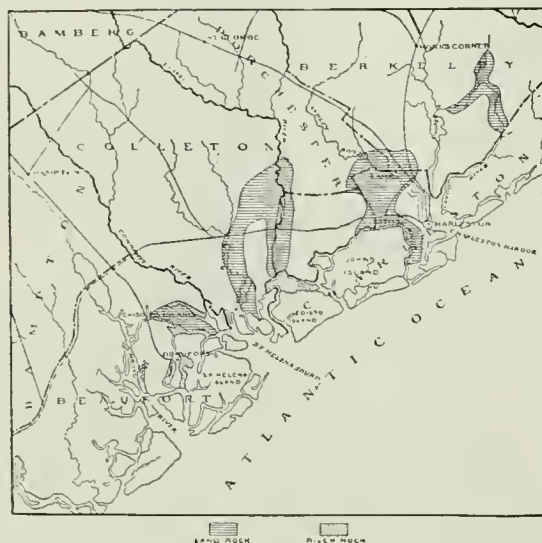


Fig. 1.

the land and marsh deposits. This report, therefore, deals chiefly with the land deposits.

GEOLOGICAL OCCURRENCE AND ORIGIN.

The phosphate-bearing stratum belongs to the Tertiary period, but geologists differ considerably regarding the exact age of the phosphate.

Toumey is of the opinion that the phosphate nodules are derived from the fragments of the Eocene marl on which the beds rest. This author, however, was unacquainted with the true nature of the phosphate. Holmes, Shepard, and Chazal also think the nodules are waterworn fragments of the Eocene marl enriched by the leaching out of the carbonate of lime and absorption of phosphoric acid from solution. These authors assign the phosphate stratum to the post-Phiocene formation. Chazal points out that it is hardly likely that nodules have derived their phosphoric acid from the animal remains with which they are mingled, since these remains themselves have been enriched by phosphatization after deposition. Levat and Brown—the latter quoting extensively from the for-

mer—agree with the above authors concerning the origin of the phosphate, but say it occurs at the Miocene horizon. Pratt thinks it belongs to an even more recent formation and that it is derived from the feces and remains of both terrestrial and marine animals intermingled with disintegrated coral and deposited in the form of a calcareous and phosphatic mud. He considers the present beds the result of fresh water rivers cutting through the phosphate strata and separating the more from the less valuable material. This author thinks the formation of these beds is still going on. Dall, from an examination of the fossils, states without hesitation that the phosphate is derived from rocks of Miocene age and thinks it doubtful if the underlying marl belongs to the Eocene.

The phosphate occurs in the form of nodules and boulders embedded in a matrix of sand, clay, and calcareous mud. The beds vary from a few inches to 3 ft. in thickness, with an average thickness of approximately 1 ft.

The nodules average from 30 to 50 per cent of the phosphate stratum, and the beds will yield from 300 to 1,500 tons of phosphate per acre, with an average of about 850 tons. The beds, as a rule, do not follow the contour of the land surface, but lie nearly horizontal. The overburden, therefore, varies considerably from place to place.

Although only the upper stratum is mined, phosphate nodules are found at more than one horizon. The following table of Prof. Shepard, published by Chazal, shows the various strata and their content of phosphoric acid.

TABLE I.—THICKNESS AND CHARACTER OF STRATA IN PHOSPHATE REGIONS OF SOUTH CAROLINA AS DETERMINED FROM A WELL.

Character of stratum.	Depth of strata. Feet.	Equivalent Content in bone of phosphoric acid.	
		Per cent.	Per cent. of lime.
Clay	17-20	0.42	0.92
Phosphatic nodules	26-30	26.79	58.48
Marl	26-30	3.07	6.70
Marl	34	3.01	6.57
Argillaceous marl	46	2.03	4.43
Phosphatic nodules	70	22.72	49.59
Argillaceous marl	85	1.26	2.74
Argillaceous marl	90	1.51	3.30
Phosphatic nodules	104	13.38	29.20
Phosphatic nodules	110-112	23.60	51.52
Argillaceous marl*	110-112	10.65	23.24
Phosphatic nodules	125-128	15.81	34.91
Hard marl	125-128	1.23	2.68
Argillaceous marl	145	traces	
Argillaceous marl	170	traces	
Argillaceous marl	228	traces	
Argillaceous marl	255	traces	
Phosphatic nodules	280	22.47	49.05
Argillaceous marl	286	.60	1.31
Marl and phosphatic grs.	287-290	5.96	13.01
Argillaceous marl	300-305	3.37	7.37
Sandy marl	305-306	.90	1.96
Sandy marl	307	.80	1.75
Hard marl	309-311	.63	1.37
Phosphatic pebbles	312-313	27.72	60.52
Hard pebbly marl	312-313	2.47	5.39
Sandy limestone	315-316	1.02	2.22
Firm limestone	321-322	.95	2.07
Sandy limestone	323	1.05	2.29

*Including phosphatic nodules.

PHYSICAL AND CHEMICAL PROPERTIES.

The South Carolina phosphates occur in nodules varying from the size of sand grains to boulders weighing several tons. The rock varies on hardness and texture from soft porous material to hard, lustrous, flintlike pieces. The nodules are sometimes smooth rounded or kidney shaped, closely resembling "coprolites," but more often they are irregular in shape, pitted, or completely perforated, the holes usually being filled with sand and clay, which has to be removed by washing. In color the rock varies from grayish white to almost jet black, and between these two extremes there are a variety of shades of red, yellow and brown.

The River Rock and that found in the marshes is usually darker in color than that found farther inland, owing probably to a larger percentage of organic matter. The rock varies in specific gravity from 2 to 2.5; and from a large number of determinations made by Shepard the average is 2.4. The nodules are usually denser and harder on their surface than in the interior, but this is not always so. After calcining, the rock becomes more brittle and can be readily and cheaply ground.

Although the South Carolina phosphate is considerably lower in grade than that from many other sources, it makes an acid phosphate of excellent quality and good mechanical condition for mixing purposes. Some farmers prefer this material to the higher grade product made from Florida or Tennessee phosphate.

The rock now marketed contains on the average about 61 per cent of bone phosphate of lime, though individual nodules and fragments are sometimes found which contain as much as 75 per cent. The following table, compiled by Chazal from analyses made by Shepard, gives the composition of South Carolina phosphate from different localities. The samples from which these analyses were made were collected during the early development of the South Carolina phosphate industry and are of somewhat lower grade than the rock which is now obtained from some of the same localities.

TABLE II.—PHOSPHATE CONTENT OF SOUTH CAROLINA PHOSPHATE ROCK FROM VARIOUS SOURCES.

Location.	Moisture. Per cent.	P ₂ O ₅ , undried basis.	Ca ₃ (PO ₄) ₂ , undried basis.	Ca ₃ (PO ₄) ₂ , dried basis.
		Per cent.	Per cent.	Per cent.
Stone River	3.68	25.61	55.91	58.04
Stone River	...	20.68	58.24	...
Stone River	1.50	25.70	56.21	57.07
Ashley River*	.00	27.01	58.95	58.95
Cooper River*	10.07	27.11	59.18	...
Chisolms Island	.84	27.26	59.51	60.00
Bull River	.79	25.14	54.88	55.32
Coosaw River	.57	27.26	59.51	59.85
Coosaw River	.66	26.78	58.46	58.85

*Land deposit.

METHODS OF MINING.

For many years the mining of South Carolina phosphate was carried on by hand labor. For a short time even the washing of the phosphate was done by hand.

The product, therefore, was at first regarded rather unfavorably, as it was not clean and produced an acid phosphate of poor quality. The early methods of mining and handling the rock have been largely supplanted by modern and more efficient methods, which turn out a clean, dry product well fitted for the manufacture of acid phosphate. Hand mining is still economically practiced where the overburden is sufficiently light and of such a character as to render the steam shovel unnecessary, but washing by hand has been entirely supplanted by the modern washer plant capable of turning out from 150 to 600 tons of clean rock every day. Hand mining is carried out as follows:

After thorough prospecting to determine the extent and value of the phosphate property, a ditch is dug through or alongside the tract to be mined and below the level of the phosphate stratum. Laterals drain into this ditch from the phosphate trenches, which are thus kept comparatively dry. A main line of railroad is established, and spurs from this are run out to the phosphate trenches in such a way that the material can be loaded easily into flat cars and hauled cheaply to the washer plant.

Hand mining is usually performed on contract, a certain price being paid for the rock delivered at the washer. The contractor in turn pays the laborers by the task, assigning each man a section of the phosphate property, from which he removes the overburden and digs out the phosphate and loads it on the cars. Where the overburden is 8 feet or more in thickness steam shovels are employed to remove it. This machine digs a canal about 20 feet wide, depositing the overburden on one bank, while a hoist equipped with a single grab bucket, or a series of buckets to be loaded by hand, runs on a track on the opposite bank of the canal. As fast as the steam shovel removes the overburden from the deposit the hoist is used to place the phosphate thus exposed on the cars. When the limit of the deposit is reached the steam shovel returns, dredging out a canal adjacent to that already dug and depositing the overburden in the old ditch. Many deposits which could not be economically worked by hand are now rendered valuable by the advent of machine mining.

WASHING THE ROCK.

After the washing of the material by hand had been abandoned as entirely inadequate and inefficient, log washers similar to those now used in Florida were introduced. The matrix in which the South Carolina phosphate is embedded, however, is of such a loose character that an elaborate cleansing process is unnecessary so that log washers have been supplanted. By the present method the rock is scraped into a hopper, which discharges into a mechanical conveyor composed of units holding one-half ton each. It is carried to the top of the washer, where each unit of the conveyor is automatically discharged, and a stream of water washes its contents down to a crusher. From

the crusher it is discharged through troughs into the lower end of several cylinder washers, which vary in number from two to eight, depending upon the size of the plant. Each cylinder is 27 ft. long and 5 ft. in diameter, the discharge end being 14 ins. higher than the end where the phosphate material enters. The first part of the lower end and the last 2 ft. of the upper end are composed of heavy wire screen, having perforations of a dimension $3/16$ by $3/4$ in.

The interior of the cylinders is fitted with plates arranged in the form of a spiral so that they throw the phosphate forward and toward the upper end as the cylinder revolves. A 2-in. stream of water under a pressure of 60 lbs. to the square inch is played upon the phosphate material from the upper end of the cylinder. This washes the sand, clay, and finely divided phosphate down to the lower end of the cylinder where it escapes through the screen and then flows out through a trough to the wash heap, which is usually located at some distance from the plant. The washed rock falls from the upper end of the cylinder upon a rubber-coated belt 26 to 30 ins. in width, along which it is carried to the wet bins. Pickers are stationed along this belt for the purpose of removing clay balls, marl, and any other foreign material which may be mixed with the phosphate. From the wet bins the rock is drawn into cars and sent to the drying sheds, where it is burned on racks of wood. About 6 cords of wood are required to dry 100 tons of phosphate from a moisture content of 15 per cent down to a moisture content of 0.5 per cent.

COST OF PRODUCTION.

Unfortunately for the South Carolina phosphate industry, the cost of production has increased without a corresponding advance in the price of phosphate rock. Indeed, the price of this material is now so low that the smaller operators in these fields have entirely ceased mining.

The increased cost of mining is largely due to the practical exhaustion of the more accessible deposits. It is now frequently necessary to remove an overburden of 15 to 20 feet in order to uncover the phosphate stratum, where formerly there were hundreds of acres of rock lying practically at the surface or covered by only a foot or two of soil.

The price of labor has also advanced from 30 to 50 per cent, and frequently it is so difficult to obtain hands that the output of rock is seriously curtailed. The equipment of a modern phosphate plant is both elaborate and costly. Steam shovels for excavation, grab buckets and hoists for taking out the rock, many miles of steel rails, locomotives and flat cars for haulage purposes, heavy machinery for washing the rock, and large sheds for drying and storing the product are essential parts of the present mining system.

On account of the topography of the South Carolina coast, weather and tide conditions affect the output of phosphate rock. In rainy weather or when the tide is very high the trenches are continually filling

with water, the banks caving in and the continual use of pumps is necessary to make mining possible. The output of rock under such conditions is often cut in half, thus practically doubling the cost of mining per ton.

These numerous and widely varying factors make it very difficult to strike an average for the cost of producing high-grade South Carolina phosphate, but the following figures, compiled from data obtained in these fields and from the author's own observation, are probably as close approximations as can be obtained.

TABLE III.—AVERAGE COST PER TON OF PRODUCING SOUTH CAROLINA PHOSPHATE.

Item.	Expense.
Labor in mining.....	\$1.50
Labor on washer.....	.10
Labor on dryer.....	.05
Haulage	.30
Fuel for power plant.....	.04
Fuel for drying rock.....	.12
Interest on investment.....	.40
Insurance	.05
Taxes	.05
Overhead charges	.10
Depreciation	.75
Total	\$3.46

WASTE MATERIAL.

In mining and preparing South Carolina rock for the market the same sources of waste are encountered as in the production of Florida phosphate. The loss of finely divided phosphate (held in suspension and passing through the cylinder screens) incident to the present method of cleaning the rock is very great, though not as great proportionally as the loss in washing the Florida product. The phosphate stratum will yield on an average about 40 per cent phosphate rock; the remaining 60 per cent, consisting of sand, clay, and finely divided phosphate, is discharged upon the waste heap. An analysis of material from the dumps made by the Bureau of Soils showed a content of about 13 per cent bone phosphate of lime, which means that over 20 per cent of the phosphate taken from the mines is discarded. Another, though minor, source of waste is at the picking board or belt where the clay balls, marl, etc., are removed by hand. Inexperienced and careless pickers frequently throw away much good material.

DISPOSAL OF PRODUCT.

Although some specimens of South Carolina rock contain as high as 75 per cent of bone phosphate of lime, the average grade of the marketed product is about 61 per cent. Almost the entire output is sold in the state on a guaranty of 60 per cent of bone phosphate and made into acid phosphate by the local factories. The present price of South Carolina rock f. o. b. at the mines is about \$4 per ton.

Some rock is shipped to neighboring states and a small amount as far north as Richmond, Va., but the freight rates will hardly admit of its shipment any great distance. The price of the higher grade Tennessee and Florida phosphate f. o. b. at the mines is so much lower that they can be delivered in Charleston, S. C., at a price but little above that of the local

product. Finely ground South Carolina phosphate has been tried a number of times on the soils of South Carolina and Georgia. But little success has been reported, although the increasing use of this form of phosphatic fertilizer in the Middle West indicates the desirability of further investigation.

EXTENT OF OPERATIONS.

The South Carolina phosphates (Land and Rover Rock) have been extensively mined in a number of localities—on both sides of the Ashley River, on the banks of the Stono River and in the stream itself, south of the Ashepoo River on Chisolms and Williams Islands, and in the Coosaw and Beaufort Rivers.

The most productive area of Land Rock has been what is known as the Ashley River Beds, which lie on both sides of the Ashley River, extending more or less uniformly over an area of about 200 square miles. Most of the River Rock marketed in past years was dredged from the Coosaw River, but mining operations there have been discontinued, owing to the depletion of the rich beds of phosphate and to the inability of the mining company to pay the royalty required by the State.

PRESENT CONDITION OF THE INDUSTRY.

The present condition of the phosphate industry in South Carolina is not good. The increased cost of mining, together with the low price of the product, has forced the small operator either to abandon his plant or to sell to the larger companies.

There are at present only two concerns engaged in mining South Carolina phosphate, and these are operating a total of four washer plants. The largest of these washers is at Lambs, on the Ashley River. Two smaller ones are located on the Stono River, about 9 miles west of Charleston, and the fourth is at Chisolms Island, Beaufort County. The total output of rock in 1911 was, according to the United States Geological Survey, 169,156 tons.

FUTURE OF THE INDUSTRY.

Those interested in phosphate mining are rather discouraged at the outlook in South Carolina.

There is little indication of any immediate rise in the price of rock, and the cost of preparing the phosphate for the market leaves such a narrow margin of profit that mining is only made commercially practicable by the use of up-to-date machinery capable of handling large quantities of material. Adverse weather or labor conditions decrease the margin of profit.

Contrary to general opinion, however, the South Carolina fields are far from exhausted. Thousands of acres of good phosphate land still remain unmined, and though the overburden on much of this property is rather heavy, improvements in mining methods will some day render it all available for fertilizer purposes.

An estimate of the actual quantity of phosphate still remaining in South Carolina is necessarily rough, for, though some of the lands have been thoroughly prospected, large areas have not been touched. Chazal, in 1904, estimated the quantity of South Carolina

phosphate still available at from 9,000,000 to 11,000,000 tons. Since that time less than 2,000,000 tons of rock have been marketed, which would leave between 7,000,000 and 9,000,000 tons. Chazal's estimate seems quite conservative, and the author is inclined to place the available tonnage somewhat higher. Suffice it to say, however, that these South Carolina fields can continue to produce rock at the present rate for many years to come.

SUMMARY.

The South Carolina phosphates were the first important deposits discovered in this country. They have been worked since 1868, and for many years produced most of our supply of phosphatic fertilizer.

The phosphate region lies along the coast in a belt extending from the Wando River, in Charleston County, to the Broad River, in Beaufort County. The rock is of Tertiary age and is usually divided into two classes, namely, the land deposits and the river deposits. These classes, however, are practically identical, the latter being merely the former washed into the river beds.

The rock is mined by first removing the overburden, either by hand or by steam shovels, and then digging out the phosphate stratum thus exposed. The rock is embedded in a matrix of sand and clay, which is removed by a washing process. During this washing much phosphate is discharged and lost in the detritus. The washed rock is afterwards dried by burning on ricks of wood.

With the exhaustion of the more accessible deposits and the discovery of higher grade phosphates in Florida and Tennessee, the output from South Carolina has fallen off considerably. River mining has entirely ceased, and only two companies are mining the Land Rock. The total output in 1911 was 169,156 tons.

The average cost of producing South Carolina phosphate for the market is about \$3.46 per ton. This is so little below the present selling price of rock that the rock can not be profitably shipped. Most of it is therefore used locally in the manufacture of acid phosphate.

The general opinion has been that the phosphates of South Carolina are practically exhausted. This is far from being the case. There are thousands of acres of rich phosphate land still practically untouched. Although the phosphate on much of this property is covered by a heavy overburden, more efficient mining methods and improved market and transportation conditions would render it all available.

The U. S. Civil Service Commission, Washington, D. C., announces an open competitive examination for technical assistant in pharmacology, for men only. From the register of eligibles resulting from this examination certification will be made to fill vacancies in this position in the Division of Pharmacology, Hygienic Laboratory, Public Health Service, at salaries ranging from \$1,800 to \$2,000 a year.



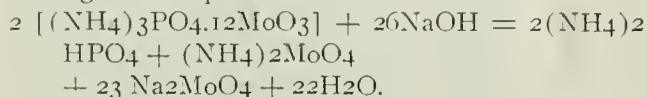
METHODS OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR INSTITUTE OF TECHNOLOGY.

Laboratory Standard Solutions—Continued.

In laboratories where iron and steel or iron ores have the phosphorus content determined by the so-called "acid-alkali" methods, solutions of nitric acid and sodium hydroxide especially prepared for that purpose are very convenient. In some cases as when a large part of the work of the laboratory is iron and steel analysis it is worth while to make the solutions exactly equivalent to each other volume for volume, and to adjust the solution of alkali so that, for example, the alkali solution may be equivalent to 0.005% of phosphorus per cubic centimeter on a two gram sample. Ordinarily it is much simpler to standardize a solution of about the desired strength and calculate a factor which when multiplied by the number of cubic centimeters used, will give the percentage upon a given weight of sample.

The method, as commonly used, consists in decomposing the material with nitric acid, or with hydrochloric acid, which is then replaced by nitric, removing all silica, precipitating ammonium phosphomolybdate under very definite and carefully observed conditions, filtering off the yellow precipitate, freeing it from all iron and then from all acid by washing with 1% HNO_3 and then 1% KNO_3 , and finally dissolving the precipitate in standard sodium hydroxide and titrating the excess of alkali with the standard nitric acid. The method is very convenient and rapid and yields satisfactory results, although it has the fundamental defect that all of those methods which measure ammonium phosphomolybdate either volumetrically or gravimetrically possess: i. e., the composition of the yellow precipitate is not either perfectly definite or perfectly constant. Consequently, the best results can only be obtained through the exercise of great care in preserving constant and definite conditions both in standardization and in determination.

The composition of the yellow precipitate is represented very nearly by the formula $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$. This is dissolved by sodium hydroxide according to the equation:



31 23(40) and the ratio

from this, 2P, is equivalent to 46 NaOH (1P = 23NaOH), between reacting weights of the two is

31 : 920.

From this equation one may calculate the strength of a sodium hydroxide solution required in order that 1 c.c. of it may represent 0.005% P on a two gram sample of material. The calculation follows:

Since the solution is to have such a strength that 1 c.c. = 0.005% P on a 2 gram sample, then the solution must be equivalent to $0.0005 \times 2 = 0.001$ gm. of phosphorus per c.c. or 0.1 gm. per liter. The weight of NaOH corresponding to this is calculated from the ratio expressed in the equation, thus:

$$\begin{aligned} 31 : 920 &:: 0.1 : x \\ 0.1 \times 920 & \\ x &= \frac{92}{31} = 2.9677 \text{ gm. NaOH per liter.} \end{aligned}$$

If a tenth normal solution of NaOH (4 gms. per liter) is at hand, it may be diluted with the proper volume of water as follows: If 1000 c.c. of the N/10 solution contains 4.0 gms., the volume to which a liter would have to be increased in order to give the required strength would be x in the proportion

$$\begin{aligned} 4 : 2.9677 &:: x : 1000, \\ x &= 1347, \end{aligned}$$

and $1347 - 1000 = 347$ c.c. must be added to each liter in order to give a solution which is equivalent to 0.005% P on a two gram sample.

If a tenth normal solution is not at hand, a solution containing approximately 3 gms. per liter is prepared and standardized, and then diluted as above to the required strength.

A solution of nitric acid of about equivalent strength is then prepared, and its strength in terms of the alkali solution determined by titration.

It may then be diluted to match the alkali volume for volume or its equivalent in terms of the alkali solution used. Phenolphthalein is used as indicator in all titrations, so a solution previously standardized with methyl orange as indicator should be restandardized using the former.

The calculation for the nitric acid solution follows: Concentrated nitric acid has a sp. gr. of 1.42, and is nearly 70% HNO_3 , so it contains per c.c. 0.7×1.42

$$= 1 \text{ gm. per c.c. (about). Since } \frac{63}{\text{HNO}_3} + \frac{40}{\text{NaOH}} =$$

$\text{NaNO}_3 + \text{H}_2\text{O}$, and the weight of NaOH per liter is 2.9677 gm., then the weight of nitric acid for a liter of equivalent solution is x in the proportion

$63 : 40 :: x : 2.9677$. $x = 4.67 +$ gms. HNO_3 , which is equivalent to 4.67 c.c. of concentrated nitric acid per liter; 5 c.c. should be used, so that the solution may be diluted if desired.

The solution of NaOH with its accompanying acid as standardized above, by calculation from its reaction with the "yellow precipitate" will give fair results, but in every case it is better to make a direct standardization in terms of phosphorus. Either of the following two methods is good:

(1) For iron and steel, iron ore, or other materials low in phosphorus.

About 0.5 gm. of Na_2HPO_4 (equivalent to about 0.11 gm. P) is dissolved in 100 c.c. of water in a 400 c.c. Erlenmeyer flask. To it is added $\frac{5}{8}$ c.c. of nitric acid and about 35 c.c. of a 30% solution of ammonium nitrate, and the whole heated to about 80°C .; 150 c.c. of a 3% ammonium molybdate solution is heated similarly and added, slowly, and with constant stirring, to the contents of the flask. The latter is then stoppered and the whole shaken for several minutes, allowed to stand 15 minutes, and the supernatant liquid poured off. The precipitate is filtered upon a hardened paper, washed first with a dilute ammonium nitrate solution acid with nitric acid, then with a 1% nitric acid solution and finally with alcohol until the washings are neutral. It is then dried at 100 to 105°C . This procedure gives about three grams of ammonium phosphomolybdate $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$, which corresponds in composition to the precipitate as formed in the process of determining phosphorus. It contains 1.65% P.

Portions of 0.25 gm. each of the dried precipitate are weighed out and dissolved in 50 c.c. of the NaOH solution from a pipette, and 2 drops of phenolphthalein added.

After complete solution the excess of alkali is titrated with the nitric acid solution and the net volume of alkali solution calculated.

0.25 gm. yellow precipitate $\times 0.0165 = 0.04125$ gm. P.
 $\frac{0.04125}{\text{net. c.c. of NaOH sol.}} = \text{phosphorus standard.}$

The phosphorus standard desired was 0.0001 so that 1 c.c. might represent 0.005% P on a 2 gm. sample. So, if the standard as obtained by experiment is divided by 0.0001, the resulting factor, when multiplied by the number of c.c. of solution used in the titration of the phosphorus in a 2 gm. sample, and then multiplied by 0.005, will give the per cent of phosphorus. The solution, after standardization, may be diluted to exact strength if desired.

It will be observed that a burette full of solution (50 c.c.) corresponds to about 25% of P. If the materials are thought to contain more than this amount, the sample should be cut down, thus increasing the percentage proportionally, for a given volume of solution used.

(2) The second method of standardization is particularly adapted to iron and steel work. It consists in the titration of the yellow precipitate obtained from a sample of standard iron or steel (as supplied by

U. S. Bureau of Standards), by exactly the same method employed in the determination of phosphorus in the sample of unknown content.*

Assume a standard iron containing say 0.114% P. A 2 gm. sample then, contains $2 \times 0.00114 = 0.00228$ gm. P. This figure, divided by the number of cc. used, gives the standard.

The same standard solutions may be used in the determination of phosphoric acid in fertilizers, a smaller weight of sample being taken to correspond to the higher percentage of phosphorus.

Acid and Alkali Solutions for the Nitrogen Determination.—When many determinations of nitrogen in more or less constant material are made, as is the case in laboratories doing routine fertilizer or food work, acid and alkali solutions of such strength that the burette reading or a simple fraction of it may give a direct reading in per cent of the substance sought, are very convenient. The standardization of such solutions for use in fertilizer analysis is a typical case.

The method employed for the determination of nitrogen in fertilizer is always some modification of the Kjeldahl process. The final measurement of the nitrogen as ammonia by titration, after the distillation, is, of course, independent of the particular process of digestion employed. It consists simply in distilling off the ammonia, absorbing it in a known volume of standard acid, and titrating the excess of acid by means of a standard alkali.

If the acid and alkali solutions are equivalent to one another c. c. for c. c., the difference in volumes will give directly the volume of acid used by the ammonia.

A fertilizer will usually contain not more than 10% of nitrogen, although some fertilizer materials such as tankage, dried blood and Chili saltpeter may contain up to 15%. The following calculation is based upon a gram sample of material containing nitrogen equivalent to not over 10% ammonia, and when materials of greater nitrogen content are to be run the sample should be decreased to half of that usually used, and the final result multiplied by two. The results of the nitrogen determination in fertilizers are usually expressed in terms of per cent NH_3 .

The Calculation.—To prepare solutions of acid and alkali so that each c.c. of acid used may give, when divided by four (4), the per cent of ammonia, on a one gram sample:

If the sample contained nitrogenous compounds equivalent to 10% ammonia, acid must be used sufficient to neutralize 0.1 gm. NH_3 , with some acid in excess. This acid should be contained in 50 c.c. of solution, which may be measured for use by means of a

*For the method of precipitation of ammonium phosphomolybdate see this journal, Vol. XVI, p. 201, or any standard work on the subject. The precipitate as obtained is washed first with 1 per cent nitric acid until free from iron, then with 1 per cent KNO_3 until free from acid, and finally treated, with the paper, with 50 c.c. of NaOH solution, rotated a few moments, and the excess of alkali titrated with the acid solution. The main thing is to preserve the same conditions in determination and in standardization.

pipette. Let, then, 40 c.c. of acid solution be equivalent to 10% NH_3 on a 1 gm. sample, or equivalent to 0.1 gm. NH_3 .

$$\frac{17}{36.45}$$

Since $\text{NH}_3 + \text{HCl} = \text{NH}_4\text{Cl}$,

then $17 : 36.45 :: 0.1 : x$ — $x = 0.2144$ gm. of HCl in 40 c.c., or 0.00536 gm. HCl per c. c., equivalent to 0.1468 times normal.

A solution of approximately this strength is made up (13 c.c. of concentrated acid per liter will give a slightly stronger solution) and standardized, by precipitating the chlorine as AgCl by silver nitrate.† From the accurate standard so obtained, the exact volume of water per liter to be added in order to get the strength required, is calculated, and that amount added for each liter of solution. All volume measurements must be accurate. After dilution, the standard should be rechecked by weighing silver chloride, as before.

Having the acid solution, it remains to prepare a solution of alkali which will exactly correspond to it, volume for volume. This may be sodium or potassium hydroxide or ammonia. In any case, a solution slightly stronger than theoretically equivalent strength should be prepared, and titrated against the acid solution. From the ratio between the two, the amount of water to be added per liter of alkali is calculated, and this added. The two solutions should match exactly. If NaOH or KOH is used, lackmoid is the most generally satisfactory indicator. For ammonia, cochineal.

Solution of such strength as to give direct or simple multiples of direct percentages from the burette readings, may be prepared in a similar manner for nitrogen or for proteids in foods.

For the general analytical laboratory the usual half, quarter, or tenth normal solutions are employed for the nitrogen determination, the use of the stronger or weaker solution depending upon the amount of nitrogen in the material. The tenth normal solution will be used the more frequently, as percentages of nitrogen are usually low.

Since the reaction which measures the amount of nitrogen is

$$\frac{17}{36.45}$$



$$\frac{36.45}{17} \quad \frac{17}{14}$$

then, 1 HCl is equivalent to 1 NH_3 , and to 1 N .

Therefore 1 c.c. $\text{N}/10$ $\text{HCl} = 0.0017$ gm. NH_3 and 0.0014 gm. N . Proteid is usually taken as $\text{N} \times 6.25$.

Of course, if the acid solution is not exactly tenth normal, the above values are multiplied by the factor. An example of the calculation follows:

Sample of material, 1 gm.

Standard HCl is $\text{N}/10 \times 0.951$.

Standard NaOH is $\text{N}/10 \times 1.014$.

Total $\text{HCl} = 50$ cc. $= 50 \times 0.951 = 47.55$ c.c. $\text{N}/10$ HCl .

Total $\text{NaOH} = 23$ c.c. $= 23 \times 1.014 = 23.30$ c.c. $\text{N}/10$ NaOH .

$47.55 - 23.3 = 24.25$ c.c. HCl used by the ammonia. Since 1 c.c. $\text{N}/10$ $\text{HCl} = 0.0017$ gm. NH_3 and 0.0014 gm. N , then

$\text{NH}_3 = 0.0017 \times 24.25 = 0.403$ gm. $\text{NH}_3 = 4.02\%$,

$\text{N} = 0.0014 \times 24.25 = 0.0340$ gm. $\text{N} = 3.40\%$,

and proteid $= 3.4 \times 6.25 = 21.25\%$.

ANALYSIS OF LINSEED OIL.

By E. C. PAILLER.†

The aim of this article is to have all the constants of linseed oil as they are in one and the same oil and to make such recommendations as are necessary. The four oils were purchased in the open market—Nos. 1 and 2 at paint dealers and Nos. 3 and 4 at drug houses, and were guaranteed to be pure raw linseed oils.

Specific gravity.—The specific gravity of the oil is taken in a 50 cc. Pycnometer at 15.6°C .

(1) .9338. (2) .9343. (3) .9339. (4) .9348.

Turbidity and Foots in Cc.—25 cc. of unfiltered oil was allowed to stand 14 days in glass tubes—one centimeter in diameter. The tubes were supported in an upright position and stood in a light place at an average daily temperature of 81.9°F .

(1) 0.59. (2) 0.20. (3) 0.17. (4) 0.58.

Breaking Test.—12 cc. of filtered oil was heated in a test tube $5/8 \times 6$ over a free flame to 300°C .

(1) Breaks at 270°C . (2) Does not break. (3) Does not break. (4) Breaks at 265°C .

Moisture and Volatile Matter (Per Cent).—The samples were dried in 4 oz. Erlenmeyer flasks at 105°C . in a current of pure dry CO_2 . 2.0 gm. of unfiltered oil was used, drying to constant weight. Samples Nos. 1, 2, 3 were constant after two hours and No. 4 after four hours.

(1) 0.02 per cent. (2) 0.03 per cent. (3) 0.34 per cent. (4) 0.23 per cent.

Ash.—10 gm. of unfiltered oil were ignited in platinum dish in a muffler at dull red heat.

(1) 0.139 per cent. (2) 0.031 per cent. (3) 0.033 per cent. (4) 0.190 per cent.

Drying Test on Glass in Hours.—Glass plates 7 ins. sq. and 1.5 to 3 mm. thick were dried at 110°C ., and the oil applied while the glass was still warm; after cooling one hour in a dessicator the plates were weighed and sufficient oil added to make 0.1 gm. The plates were kept under a ventilated bell jar in a light place. Drying was completed at an average daily temperature of 77°F . without a damp day intervening.

(1) 60 hrs. (2) 54 hrs. (3) 69 hrs. (4) 54 hrs.

Oxygen Absorption.—Lead dishes 3 ins. in diameter

†See this journal, Vol. XI, No. 1 (Feb., 1914).

†Department Public Works, Bureau of Highways, Manhattan Borough, New York City.

and $\frac{3}{4}$ in. in height were used in the place of aluminum dishes. After completion of test the dishes all appeared clean and bright.

(A) 5 gm. litharge.

%	hrs.	%	hrs.	%	hrs.	%	hrs.
13.18	141	11.31	141	11.75	141	12.69	141

(B) 10 gm. litharge.

13.75	141	13.29	141	12.78	141	13.40	141
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The detailed results are presented in Table I:

TABLE I.

Time in hours.	Oil No. 1. 10 Gm. 5 Gm.		Oil No. 2. 10 Gm. 5 Gm.		Oil No. 3. 10 Gm. 5 Gm.		Oil No. 4. 10 Gm. 5 Gm.	
	PbO.	PbO.	PbO.	PbO.	PbO.	PbO.	PbO.	PbO.
24.....	12.89	12.04	11.98	8.58	11.81	10.31	12.49	11.01
45.....	12.39	12.04	11.75	9.29	11.44	10.31	12.09	11.16
53.....	12.52	12.04	11.85	9.48	11.57	10.50	12.15	11.28
69.....	12.70	12.25	12.18	9.93	11.81	10.75	12.40	11.59
77.....	12.95	12.52	12.37	10.25	12.00	11.04	12.69	11.90
117.....	13.16	12.66	12.68	10.81	12.26	11.31	12.89	12.16
125.....	13.39	12.97	12.85	10.96	12.45	11.46	13.09	12.35
141.....	13.74	13.18	13.29	11.31	12.78	11.75	13.40	12.69
149.....	13.45	13.07	13.00	11.20	12.54	11.63	13.18	12.48
165.....	13.24	12.79	12.79	10.99	12.30	11.37	12.97	12.20
173.....	13.19	12.75	12.79	11.01	12.30	11.37	12.97	12.20
189.....	13.16	12.73	12.81	11.11	12.28	11.42	12.93	12.21
197.....	12.97	12.60	12.64	10.98	12.09	11.18	12.72	12.09
213.....	13.12	12.66	12.81	11.09	12.28	11.44	12.89	12.20
221.....	13.49	12.99	13.17	11.43	12.61	11.69	13.23	12.50
309.....	13.47	13.07	13.31	11.62	12.59	11.69	13.21	12.59

Oil taken 0.5165 0.5157 0.5205 0.5374 0.5374 0.5225 0.5273 0.5328

Acid Value.—(Expressed in Mg of KOH per gm.):

1.20	3.60	2.50	1.40
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Saponification Value.—(Expressed in Mg of KOH per gm.): Saponification was effected by boiling one hour under a reflex condenser and corrections were applied for the action (on glass) by the alkali:

190.6	190.4	190.6	190.2
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191.0	189.9	190.8	190.2
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Lieberman's Starch Test.—

Negative.	Negative.	Negative.	Negative.
Green.	Green.	Green.	Green.

Refractive Index.—In this determination the Ziess Refractometer was used, a Sodium light as a source of illumination being used. Determinations were made on the original oils and on the fatty acids prepared from the oils:

(A) Original oils at 25°.

(1) 1.4799	(2) 1.4793	(3) 1.4794	(4) 1.4797
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(B) Fatty acids at 25°.

(1) 1.4710	(2) 1.4703	(3) 1.4708	(4) 1.4704
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Acetyl Value.—20 cc. of the filtered oil were boiled with an equal volume of acetic anhydride for 2 hours, under a reflex condenser, the flask being ground to the condenser. Both distillation and filtration methods were used.

(A) Distillation method:

28.3	21.0	18.5	18.3
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30.3	36.0?	18.8	20.3
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(B) Filtration method:

29.0	23.0	45.0	40.9
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21.5	21.3	39.2	34.3
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In the Distillation method, it appears that the results are fairly uniform, omitting the 36.0 value for oil No. 2. However, in the Filtration method the results

are far from satisfactory. From my experiments it seems that these discrepancies are due to free fatty acids coming through with the final filtrates, as indicated by the fact that the more turbid the filtrate the higher is the result obtained. In the results given under "B" after adding the correct amounts of standard acid to the soap solution, the resulting solutions were heated under a reflex condenser until quite clear and then filtered. Even this procedure did not yield perfectly clear filtrates. In one case, where the filtrates were fairly turbid, a value of 36.3 was obtained from oil No. 1. In another case, where the filtrate was markedly turbid, a value of 55.6 was obtained for oil No. 2. These results were excluded for this reason.

Lewkowitch (Chem. Tech. and Anal. of Oils, Fats and Waxes, Vol. 1, 1904, page 270) makes the following statement:

"In order to facilitate the separation of the insol. fatty acids in the filtration process, it will be found useful to add a slight excess of mineral acid. Of course this amount must be measured accurately and deducted from the alkali required for determining the dissolved acids."

I made no determination by adding more than the equivalent quantity of acid, but it seems that work in this direction would be of some value in the filtration method.

Hexabromide Test.

(A) Bromine precipitate (Tohman's method):

(1) 55.93	(2) 57.01	(3) 58.48	(4) 49.31
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(B) Melting point of bromine precipitate:

(1) 137° C.	(2) 138° C.	(3) 138.5° C.	(4) 136° C.
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In addition to the above determination, the Hexabromides of the fatty acids were also determined according to the method of Hehner and Mitchell, as described in Lewkowitch (Chem. Tech. and Anal. of Oils, Fats and Waxes; Vol. 1, 1904, Page 365):

(C) Hexabromides of fatty acids (Hehner and Mitchell):

(1) 35.08	(2) 31.79	(3) 36.31	(4) 35.46
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My experience with this determination leads me to believe that the volumes of reagents used is of importance. The following series were conducted as follows:

Thirty-one cc. of glacial acetic acid were added for every gram of fatty acids used, adding bromine in excess. After standing for 3 hours in the refrigerator the bromides are filtered through a Gooch crucible and washed successively with 5 cc. each of chilled glacial acetic acid, ethyl alcohol and ethyl ether. The crucible is dried one hour at 100° C. and weighed. The results obtained are given under "D."

(D) Hexabromides of fatty acids (Hehner and Mitchell):

29.94%	28.16%	30.41%	31.29%
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29.87%	27.38%	29.75%	31.54%
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(E) Melting point of Hexabromides of fatty acids:

178°	178.5°	178.3°	178.4°
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Inasmuch as the bromides were not pure white, as obtained above, another series of determinations were made, in which the bromides were washed with a still further quantity of ethyl ether until pure white. The results are given under "F."

(F) Hexabromides of fatty acids (Hehner and Mitchell), washed until pure white:

28.33	26.92	27.67	28.79
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A larger quantity of Hexabromides of the fatty acids were prepared quantitatively and washed until pure white. The melting points are given under "G."

(G) Melting points of Hexabromides of fatty acids:

177.3	177.8	177.3	177.7
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It is evident from these results that the determination as carried under "D," with the exception of the 32.51% on oil No. 3, show quite uniform results, and it is my opinion that a further study along these lines is of extreme importance.

Iodine Number.—

(A) Hanus method:

181.1	182.1	185.3	183.6
185.4	182.1	184.0	183.8

(B) Wij's method:

187.3	183.9	186.9	184.6
187.2	184.4	187.1	185.8

In both the Hanus methods the solution of the oil was allowed to remain in contact with the reagent, in a dark place, for one hour before titration.

The U. S. Consul General at Berlin reports that an active competitive struggle has broken out in Germany between two groups of manufacturers of sulphate of ammonia, comprising the German ammonia combination of Bochum on one side and the well-known Ludwigshafen firm on the other.

The Bochum concern is a combination of gas and coke concerns which produce sulphate of ammonia according to the usual manner, while the Ludwigshafen concern is producing it according to a new chemical method, and in order to get into the market has cut prices, being in a position, so it is stated, to produce much larger quantities if a market therefor may be found. At present the mining concerns comprised in the Bochum combination are selling the larger quantity of this product, and, as they fear future complications in the market, are now urging their buyers to sign agreements whereby the latter pledge themselves not to deal with middlemen, in return for which they are to be allowed a 10 per cent discount at the end of the year on running contracts.

The total value of fertilizers consumed in Japan in 1912 was \$104,425,093, of which \$30,617,500 was represented by artificial fertilizers, \$32,300,000 by night soil, \$31,410,000 by taibi (manure made of straw, etc.), and \$7,057,500 by ryokubi (weeds), and other kinds.

THE DETERMINATION OF PHENOL IN THE PRESENCE OF HEXAMETHYLENETETRAMINE AND FORMALDEHYDE.*

By L. V. REDMAN, A. J. WEITH and F. P. BROCK.

During a research into the rate of condensation between phenols and active methylene groups in the production of synthetic resins it became necessary for us to find a rapid and accurate method for the determination of phenols in the presence of substances containing methylene groups, e. g., formaldehyde, hexamethylenetetramine, etc.

In previous papers¹ we have described a bromination method which serves for the very accurate and rapid quantitative determination of phenol in a water solution. The method consisted in diluting the phenol to *N*/1,000, in acid solution, shaking the solution for 1 minute after the bromide-bromate solution is added, then adding KI, shaking again for 1 minute and titrating the excess iodine with thiosulphate. The whole operation was carried out at 20-25° C.

The present paper deals with the determination of phenol in a water solution in the presence of hexamethylenetetramine or formaldehyde or both, using the above method with whatever modifications are mentioned later in this paper.

The first of these probable interfering substances to be tried was hexamethylenetetramine and the results are given in Table I. Hexamethylenetetramine does not interfere in the determination of phenol by bromine when present up to 1 per cent of the total solution,² i. e., 30 mols. of hexamethylenetetramine to 1 mol. of phenol. Much larger amounts than this have been tried. As much hexamethylenetetramine as 15 per cent of the total solution, i. e., 450 mols. of hexamethylenetetramine to 1 mol. of phenol, has been added in a single determination of the phenol without changing the results. The only intermediate change noted when the hexamethylenetetramine was present in large quantities was a tendency on the part of the free iodine to form a brick-red granular precipitate, or a beautiful iridescent crystalline precipitate with the excess hexamethylenetetramine. This precipitate which is either the tetra-iodo-hexamethylenetetramine or di-iodo-hexamethylenetetramine dissolves up readily on the addition of the thiosulphate giving back the free iodine, and does not in any way interfere in the quantitative determination.

The presence of free formaldehyde, however, interferes very seriously with the phenol determination. Results that are 7-8 per cent too high are obtained when the total solution is 1 per cent formaldehyde as is shown in the table (Expts. 5 and 6). The higher the percentage of formaldehyde present the higher the

*From The Journal of Industrial and Engineering Chemistry.

¹Redman and Rhodes, Journal of Industrial and Engineering Chemistry, 4 (1912), 655; Redman, Weith and Brock, *Ibid.*, 5 (1913), 389.

²The total solution refers to the volume after the dilution has been made with the water and acid, before adding the bromide solution.

results which are obtained for the phenol present in the solution until, for 40 per cent formaldehyde, bromine is absorbed in very large quantities and no precipitation of tribromphenol takes place, and the determination of phenol by this method is quite impossible.

It is evident, then, that if hexamethylenetetramine does not interfere with the determination, and formaldehyde does not interfere, the addition of ammonia to the solution in which formaldehyde is present as an interfering substance may, by forming hexamethylenetetramine with the aldehyde obviate the trouble.

The addition of ammonia to a phenol solution containing formaldehyde was tried and the results are given in the table, Expts. 7, 8, 9, 10. If the unknown phenol solution be made 2 *N* with ammonia and the whole allowed to stand for 5 minutes, the formaldehyde is transformed over into hexamethylenetetramine or some intermediate non-interfering compound and the determination of the phenol may be made with speed and accuracy. Allowing the ammonia, formaldehyde and phenol to remain together in the water solution longer than 5 min., *e. g.*, 18 hours, before the determination is made does not affect the results as is shown in Expts. 9 and 10.

This method of determining phenol in the presence of formaldehyde would not hold if a condensing agent had been present previously or if the solution had been treated in a way which tended to form oxybenzyl-alcohol, saligeno-saligenin, etc.

In determining phenol in the presence of hexamethylenetetramine the bleaching of the starch iodide

III. The addition of strong ammonia to the phenol-formaldehyde solution forms with the aldehyde, hexamethylenetetramine or some intermediate ammonia-aldehyde product which does not interfere with the quantitative determination of phenol.

A NEW METHOD FOR DETERMINING THE VALUE OF DISINFECTANTS.*

By C. A. DUYSER and W. K. LEWIS.

Since the chief function of a disinfectant is to kill bacteria or other micro-organic growth, its commercial value may be measured in terms of either of two quantities—first, the time required for a disinfectant of definite dilution to destroy a predetermined bacterial culture; second, that certain dilution necessary to kill the bacteria of this culture in a definite interval of time. But bacteria are living organisms having more or less an individuality. Not only are there many different strains or types of each organism, but the same culture of bacteria may differ in many of its characteristics from day to day. Hence it is impossible to employ as an analytical standard for determining the killing power of disinfectants an organism which may vary in its vitality, or a culture which may be heterogeneous as to the vitality of the individual bacteria present. The other alternative is to agree upon a certain chemical compound of known composition, and which may be obtained with ease, as the standard disinfectant, and to measure all other disinfectants in terms of the killing power of this standard. Phenol is the substance more generally employed for the purpose, and the ratio of the ability of a disinfectant to kill the bacteria of a certain culture to the ability of phenol to kill the same bacteria under absolutely the identical condition is called the "Phenol-coefficient."

There are at present three methods for measuring the bactericidal value of disinfectants, all using the above principles, but differing in details of manipulation; these are the Rideal-Walker, the Lancet and the Hygienic Laboratory Methods. Each of these, however, gives unsatisfactory results, not only when carried on by different experimenters in different laboratories, but by the same operators when carrying on his work in duplicate. Blythe¹ has called attention to this fact most forcibly, and has made a strong appeal for a more chemical method for testing disinfecting materials. We believe that the methods now in use are not sound for the following reasons: The mechanism of the reaction by which a disinfectant kills bacteria is not definitely known, but it is generally conceded that the concentration of the disinfecting solution falls in proportion as the number of living bacteria present is decreased. It is possible that the number of molecules of disinfectant is so great in proportion to the number of bacteria present that the change in the concentration of the disinfectant as the

TABLE I.

No.	Amount of interfering substance.	Cc. of NH ₃ added.	Time after ammonia was added, to detn.	Cc.'s of HCl added.	Cc.'s Br. sol. used.	Thiosulfate sol. used.	Per cent of phenol determined.
1		0		6	16.92	3.42	100
2		0		6	17.10	3.59	100
3	1 gram hexa.	0		6	16.97	3.56	99.36
4	1 gram hexa.	0		6	18.68	5.17	100.19
5	3 cc. 40% CH ₂ O	0		6	17.00	2.52	106.92
6	3 cc. 40% CH ₂ O	0		6	18.46	3.70	108.32
7	3 cc. 40% CH ₂ O	10	5 min.	17	16.40	2.92	99.72
8	3 cc. 40% CH ₂ O	10	5 min.	17	15.89	2.40	99.50
9	3 cc. 40% CH ₂ O	10	18 hrs.	17	16.98	3.54	99.50
10	3 cc. 40% CH ₂ O	10	18 hrs.	17	16.62	3.16	99.51

Water of dilution=100 cc.
Phenol solution used=15 cc.
Bromide-bromate sol.=0.09970 *N*.
Hydrochloric acid=37% solution.
N/10 ammonia=28% solution.
Thiosulfate=0.09825 *N*.

color by the thiosulphate is slightly retarded by the presence of hexamethylenetetramine and it is necessary to give a few seconds after the addition of the thiosulphate to allow the blue color time to disappear.

CONCLUSIONS.

I. Phenol in the presence of hexamethylenetetramine may be determined by the method already described for the determination of phenol.

II. Formaldehyde interferes with the volumetric determination of phenol by bromine.

*From The Journal of Industrial and Engineering Chemistry.

living bacteria disappear is negligible. But it is generally true in carrying out these methods that so large a number of bacteria is used that the strength of the disinfectant is materially changed as the killing of the bacteria proceeds and before the last, or more hardy individuals are killed, the disinfectant is appreciably exhausted. Misleading results are therefore obtained.

Each of the above methods provides for removing what is supposed to be a perfectly constant volume of the culture from a tube or flask by means of the so-called standard loop. This is a circular loop made by winding a platinum wire of determined size around a rod having a definite diameter. There are so many physical conditions which apparently would influence the volume of liquid such a loop would carry that it was thought of interest to determine this volume. A strong solution of iodine of known strength served as the liquid to be transferred, and a dilute solution of thiosulphate was used to measure the amount of iodine contained in each loopful. A number of loopfuls were withdrawn with great care and placed in cold distilled water. The weight of iodine in each was then determined by titration, and from these data the volume of the loopfuls calculated. When great precautions were used, the volume of one loop varied as much as 30 per cent from the mean of 15 loopfuls, and when hurriedly done the variation rose as high as 80 per cent. The volume transferred by the standard loop is on the average 0.003 cc. It may be easily seen that if the number of living bacteria has been largely reduced by the action of the disinfectant it is very possible to transfer a loopful from the disinfected culture to a new culture tube which may contain no living bacteria, even though there are an appreciable number present. But even assuming, notwithstanding the law of chances, that each loopful contains a number of bacteria proportioned to the volume carried by the loop, since this volume may vary by at least 30 per cent from the mean, and may easily vary as much as 80 per cent, concordant results cannot be expected.

The use of a tube of sterile broth into which to transfer the loop of disinfected culture to determine whether or not all bacteria have been killed, is also unsatisfactory. If the tube should prove fertile there is no means of determining whether the inoculation was due to one stray survivor which happened to be in the loop and whose presence was accidental, or to a considerable number of bacteria which the disinfectant had failed to destroy.

To recapitulate, the present methods are unreliable because: (a) The use of an excessive number of bacteria depletes the disinfecting solution before the culture is rendered sterile. (b) An unknown volume is withdrawn for testing, in that the volume of the standard loop is not constant. (c) It is impossible to determine from the broth tube inoculated, how com-

plete the killing was at the time the sample was withdrawn.

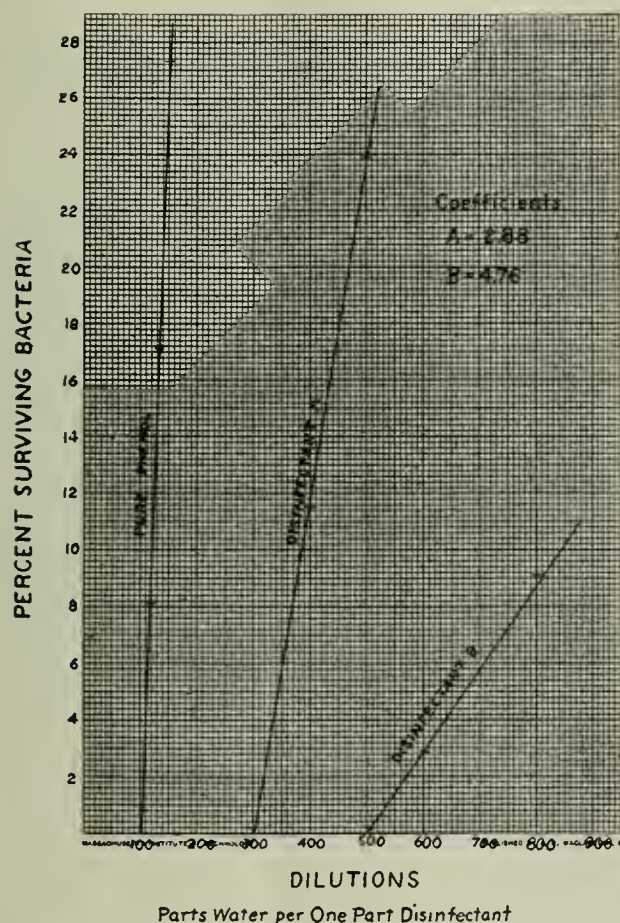
A method developed in this laboratory which seems to eliminate these sources of error, and which is not more laborious, is, in principle, as follows: The disinfectant to be analyzed for its relative bactericidal power is diluted with water to three or four definite concentrations, the extent of dilution depending upon its strength. Pure synthetic phenol is diluted in a like manner. Into a series of these known concentrations of both phenol and the disinfectant under consideration is placed an equal volume of a standard bacteria culture and the mixture allowed to remain an exact number of minutes. At the end of this time an aliquot part of each mixture is plated out in Petri dishes on nutrient agar and incubated until the colonies representing the surviving bacteria can be counted. At the same time plates of equal dilutions of the culture but without the disinfectant are incubated. The ratio of surviving organisms to the number present on the undisinfected plates is then plotted against the dilution, and two curves, one for the standard phenol and one for the disinfectant are obtained. From these the relative strength of the two disinfectants can be read off at any desired point on the curves, and a coefficient either for total killing or any determined percentage of killing may be calculated.

The exact manipulation recommended is as follows: One gram of the disinfectant to be analyzed is weighed accurately and diluted with sterile water to a volume of 100 cc. From this stock solution a series of dilutions is made. Since an equivalent part of each of these is later to be mixed with an equal volume of a dilute water suspension of bacteria, the strength of the series should be twice that of the final dilution desired. When nothing is known of the relative strength of the disinfectant in hand, dilutions of one part disinfectant in 200, 400, and 800 parts sterile water have been found advisable. From a 5 per cent solution of synthetic phenol a series of dilutions of one part phenol to 100, 125 and 150 parts water will give a curve covering a considerable range of killing when *B. coli communior* is used. Tubes of sterile broth and nutrient agar culture medium are prepared according to the standard methods, and a number of 10 cc. and 1 cc. pipettes and ordinary test tubes are provided.

Ten cc. of each of the dilutions of disinfectant and phenol are added to properly marked test tubes and placed in a water bath at 20° C. Ten cc. of a broth culture of *B. coli*, so diluted with sterile water that 1 cc. contains from 20,000 to 60,000 bacteria, are placed by means of a straight graduated pipette in test tubes, one more than the number of disinfectant and phenol tubes just described, and these are also placed in the water bath. This is a twenty-four hour broth culture of reaction +1, which has been transformed daily for not less than three days. When the whole has come

¹Original Communications, Intern. Cong. Applied Chem., 1909.

to a temperature of 20° C. the contents of one of the tubes of disinfectant is poured into one of the tubes of bacteria and well shaken. After one-half minute this procedure is repeated with the second tube and so on through the series. At the end of five minutes, 1 cc. is withdrawn from the first tube of disinfected bacteria and added to a bottle containing 99 cc. of sterile water; one-half minute later the second tube is so treated and the others at ½ minute intervals in the same way. To the tube of bacteria in which no disinfectant was placed, 10 cc. sterile water are added and 1 cc. is transferred to a bottle containing 99 cc. sterile water. These bottles are well shaken, and duplicate Petri dishes are poured from each one, 1 cc.



solution being first added to the dish followed by enough nutrient agar to make a satisfactory culture plate. When the dishes set they are inverted and allowed to incubate at 37.5° C. for 48 hours. At the end of this time the plates are counted and the ratio of the number of surviving bacteria to the number of colonies on the non-disinfected plate is determined. When plotted against the dilution two curves are obtained, types of which are shown on the accompanying plate. If a number of disinfectants are examined at the same time, it is of course not necessary to repeat the phenol series and the bacteria blank with each. The coefficient of total killing for Disinfectant A is seen to be 2.88, while for B it is 4.76.

A study of a large number of these plates shows that the curves for the so-called emulsion disinfectants are almost straight lines; at most there is but a slight curvature. Thus a small number of points will locate a line with a fair degree of accuracy and the necessity of using small increments of dilution as obtains in the older method is not here present. As is clearly shown in this plot, though desirable, it is not necessary, as in the other methods, that the most concentrated solution of the disinfectant used should produce a sterile tube or plate, that is, show total killing. If at least three points have been found to lie fairly well upon a smooth curve, the line may safely be interpolated until it cuts the axis representing complete killing and the coefficient calculated from this intersection. The results obtained may be duplicated with sufficient precision to warrant confidence in them. This is true not only of a single operation carrying on duplicate determinations, but by two analysts working separately.

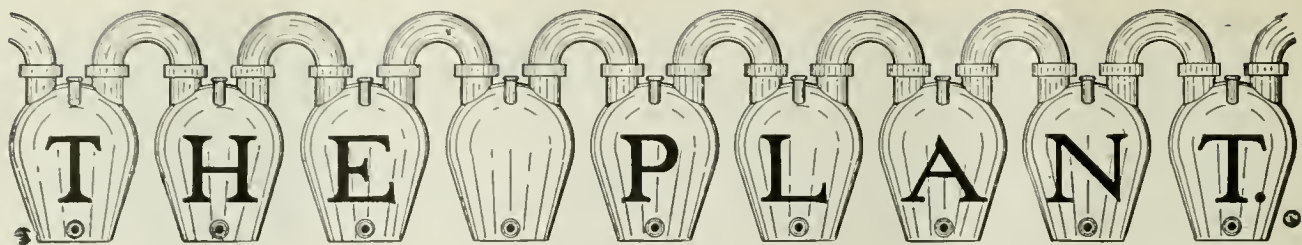
	I.	II.
1.....	1.82	4.58
2.....	5.17	5.05
3.....	6.95	6.64
4.....	9.64	9.30
5.....	4.28	4.08
6.....	2.04	2.24

The above duplicate results obtained by the same analyst will give an idea of the degree of accuracy which may be readily attained.

The quantities of sulphate of ammonia manufactured in Germany were estimated to have been 500,000 metric tons of 2,204.6 pounds in 1912, worth \$29,750,000, and 418,000 tons in 1911, valued at \$23,324,000. Of this large quantity the German ammonia combination in Bochum disposed of about 300,000 tons in 1912 and about 245,000 tons in 1911. The producing concerns in Upper Silesia, Rhineland, and Westphalia are said to be willing to engage in a competitive contest, claiming that the cost of manufacturing artificial ammonia is more than the cost of producing ammonia in the coke and gas works. The average price of sulphate of ammonia was \$59.47 per ton in 1912 and \$55.60 in 1911. It is intimated that when the contest becomes a little keener prices may fall off \$24 per ton.

German exports and imports of this article during the past three years were as follows: The total imports amounted to 24,463 tons in 1911, 23,097 tons in 1912, and 34,626 tons in 1913. Of these totals Austria-Hungary furnished 18,122 tons in 1911, 17,861 tons in 1912, and 21,203 tons in 1913. The total German exports of sulphate of ammonia in 1911 were 74,445 tons; in 1912, 56,948 tons; and in 1913, 75,868 tons. The exports to the United States amounted to 2,274 tons in 1911, 902 tons in 1912, and 5,629 tons in 1913.

The value of the 34,626 tons imported in 1913 was fixed by the authorities at \$2,266,236 and the value of the 75,868 tons exported at \$4,433,226.



RAMIE FIBER AND ITS MANUFACTURE.*

RAMIE IN THE FAR EAST.

There has been a revival of interest in the cultivation, manufacture and export of ramie fiber in the Far East which is likely to have some important results. The export of one variety of ramie in grass form (hand cleaned, but not degummed fiber) from China has been increasing steadily and the Philippine government is carrying on experiments with the two species of ramie near Manila. Whether the cultivation of the fiber in the Philippines is to be carried on in a commercial way seems to depend altogether upon the invention of a successful decorticating machine.

In the meanwhile Chinese production with Chinese methods of decorticating and degumming the fiber is greatly on the increase. Nevertheless, the only attempt to produce the fiber and manufacture it in a modern establishment in this field has so far not been a success, for reasons growing out of management rather than anything developed in the essential nature of the enterprise.

The Grass Cloth of Commerce.—In the vicinity of Hongkong—that is, at Canton, Swatow, Kiungchow and in other smaller ports in this vicinity—the fiber is produced largely in connection with the “grass cloth” or “Canton linen” trade, being produced for local manufacture into cloth, and is exported as cloth or, to a large extent, in the shape of embroideries and drawn work. The export of grass cloth itself has come to be an important item in Chinese exports, the shipments abroad in 1912 being valued at \$1,489,566, as compared with \$1,013,977 in the previous year. Curiously enough the larger portion of these exports—an average of nearly two-thirds of the whole, though not so large a portion as formerly—go to Chosen from the Yangtze Valley, especially from Kiukiang and Chungking. About 40 per cent of the total exports come from Swatow and ports south, especially Canton, Kiungchow and the Pearl river delta ports. Hongkong in 1912 received about one-third of the total exports, and a large portion of the Hongkong imports go to the United States. Grass cloth, embroidered or plain, usually white or dark blue, is one of the chief articles purchased by tourists in this part of the world.

The chief exports of ramie as fiber come from the Yangtze Valley, the districts around Kiukiang being said to produce the best fiber. There are two varieties or species of ramie the *Boehmeria nivea*, which is

grown in the temperate zones and commonly known as “China grass,” and the *Boehmeria tenacissima*, which is the true ramie or rhea. It is the former species only which is produced in China. In common with other plants, it is known as “ma,” and the plant used in South China is known as “chu ma.” In China the plant often grows more or less wild. The best is cultivated, being produced on hillsides or where there is plenty of drainage, preferably in a light, sandy soil, good drainage but plenty of rain apparently being the chief requirements for its successful production.

Area of Production—Planting and Cultivation.—The plant is produced all over China south of the Yellow river and in Indo-China, the Shan states and in India, though it is said by the Chinese here that attempts to grow the plant successfully on a commercial scale in India have not produced good fiber. Apparently there are subvarieties of the plant in China, for the characteristics of the plant vary in various portions of the country. The plant grown in the south of China is harder to strip and manipulate and usually produces coarser fiber. In the Yangtze Valley the plant usually grows about 7 ft. tall. The cultivation is usually started by planting seeds and transplanting the seedlings into prepared plots. The plants can be cut after from two to four years, apparently depending upon the nature of cultivation and the variety of the plant. After that, three cuttings a year, in this part of China at least, are had. In this part of China the second cutting is usually considered the best. Roots usually will produce plants for about ten years without replanting.

Processes of Fiber Preparation.—The Chinese method of obtaining the fiber from the plant is tedious and expensive in labor, but cost is kept down by the employment of women and children in parts of the process. The stalks are cut and stripped of the leaves and arranged in bundles according to length and size. In this part of China they are then soaked for two days in water, usually the farm pond or pool, though this preliminary soaking is said to be unnecessary in the north. At the end of this soaking the stalks are each bent or broken, usually about mid length, and the bark or fiber-producing portion is stripped off by hand. Sometimes an iron pin set in a board is used in the process. The portion stripped off is then further soaked a day or so, and it is then scraped by hand with a dull-edged short-bladed knife, being passed between the knife and the edge of a board or some similar arrangement, so as to scrape off and squeeze

*From the Daily Consular and Trade Reports.

out the mucilaginous and soft portions of the plant. By this process the fiber comes out in rolls. It is then usually washed and dried, and the fibers are partially separated by beating with a mallet on a block. In the Chinese process of preparation for weaving, the fiber is then usually picked apart by hand by women and children. The fiber exported is usually shipped before the beating process, however, though often it is hackled or combed roughly with a row of iron pins set in a board. When prepared for weaving, the Chinese in this part of China boil the fiber in limewater, alternately beating and boiling it until the desired fineness of fiber is obtained. The process varies greatly, but is, in short, a beating and boiling method of separating the fibers by removing as much of the resin and gum as possible.

The exports of fiber in this shape from all China in 1912 amounted to 178,415 piculs, or about 11,900 short tons, valued at \$1,675,697 gold, as compared with exports of 153,140 piculs, or about 10,210 short tons, valued at \$1,267,609 in 1911, and exports to the value of only \$554,937 only five years ago, in 1908. Something over half of the exports went to Japan, where the fiber is variously handled and employed, being used to some extent in the manufacture of silk cloth. France and Belgium take the greater portion of the balance, the United States taking something like \$40,000 worth a year directly at present besides that imported indirectly through Hongkong and other countries.

Failure of Modern Factory.—The attempt to manufacture the fiber in a modern equipped plant in this part of the world seems to have failed because of the indisposition on the part of the Chinese owners of the plant to employ foreign expert superintendence.

About four years ago a factory was constructed at Kowkong, a Chinese city near Kongmoon, an open port a short night's trip from Hongkong by steamer up the Pearl river. This factory was constructed through the efforts of an American representative of knitting machine interests and was equipped with machinery for handling the ramie from the plant to a finished stocking or piece of underwear. The factory was equipped with 1 softening machine, 1 filling machine, 3 dressing machines, 1 weighing machine, 3 drawing frames, 2 roving machines, 1 doubling machine and 1 twisting machine, all for the "first draft" and of English make. For the "second draft" there were 1 carding machine, 3 drawing frames, 1 roving machine and 3 spinning machines, with 900 spindles altogether, all these machines also being English. There were also 6 winding machines, 4 underwear machines, 6 stocking machines, 4 rib machines, 2 paper-box machines, 3 loopers and 8 high-speed sewing machines, all of American make.

This factory was also equipped with a French decorticating machine, but after considerable work and experiment it was found that the machine bruised

the fiber unduly, and it was discarded, and the Chinese process of cleaning the fiber by hand stripping and scraping with a knife was followed. The capacity of this plant was 900 lbs. of fine counts yarn per day, the yarn made usually running from 50s to 60s, although yarn was spun in the establishment as fine as 120s. The factory was operated for about a month by the erectors of the machinery under their guaranty and was successfully turning out finished products when the question of foreign superintendence was raised. The Chinese owners were not willing to pay the salaries necessary for expert superintendence and attempted to run the concern without it. The result was trouble with the machinery and with the special process of degumming the fiber which was followed. After a few weeks' operation the plant was shut down temporarily, and it has not resumed work, negotiations for superintendence so far having failed to result in an agreement.

Degumming Difficulties—Advantages of Factory Preparation.—The difficulty in manufacturing the fiber in this factory and elsewhere out here is in the matter of degumming the fiber. As it is stripped from the plant the fiber is hard, coarse in appearance, stiff and full of resin and gum. The factory process was more or less secret, but involved the "rotting" of the fiber by soaking it in a solution of acids and salts and boiling it at a high temperature.

The Chinese method, as indicated, is to alternately boil and beat the fiber until it is free of the gum, but the Chinese process is imperfect, and for this reason the Chinese grass cloth made from the fiber is more or less stiff and inelastic, crumples easily and remains crumpled, and otherwise shows the lack of pliability desired in a fine fabric. The factory process leaves the fiber almost as soft as cotton or silk, elastic and pliable. The fiber by either process can be bleached perfectly, will take any dye readily and has a silky luster which it retains indefinitely. Twenty per cent of the factory-made product can be mixed with silk without detection by ordinary examination. The fiber by either process is very strong and is highly absorbent, the factory-made fabrics being especially so. The degumming process in either case requires about ten days. By the Chinese process a workman can degum and prepare only 2 lbs. of fiber per day. The factory here prepared fiber at a cost of about 24 cents gold per pound and fine yarn was produced at 42 cents to 44 cents gold per pound, according to the count.

It is difficult to ascertain actual costs in the production of native cloth from the fiber, but native ramie yarn made from the fiber as beaten and boiled out and carded and spun in the rough native method probably costs about 10 per cent over the prices given. By the native process the full fineness of the fiber can not be taken advantage of since enough gum or resin remains in the fiber to prevent its complete subdivision. [Decortication is the separation of the fiber from the

woody inner portion and the outer bark, and it precedes degumming.] Samples of cloth and of knit goods made from yarn prepared by improved process show immensely greater division of the fiber and a consequently great improvement in the cloth.

Prospects of this factory at Kowkong are uncertain. The plant at present is idle and of course is rapidly deteriorating. There is disagreement among the powers as to the policy to be followed. It seems clear that the operation of such a factory, involving close technical knowledge and accurate care of details, can not be successful with native superintendence alone, at least without superintendence of highly trained experts which might be had in the training of Chinese students abroad. There seems to be no reason why the manufacture of this fiber on commercial scale in China, however, should not be a success.

Experiments in the Philippines.—The prospects of producing the fiber in the Philippines seem to be particularly good and the Philippine government has been making experiments as the basis for a comprehensive effort to induce the production of the fiber. In a statement prepared in response to inquiry as to the prospects of the fiber in the islands the acting director of the Bureau of Agriculture says:

There are two varieties, or rather species, of the so-called ramie plant, namely: *Boehmeria nivea*, commonly known as China grass, and *B. tenacissima*, known as ramie or rhea. The former species is grown in the temperate zone, while the latter is grown largely in the eastern Tropics, and is distinctly a tropical plant. These two species require practically the same methods of cultivation and fiber extraction. Their product is also identical, and so far as we know no distinction is made between them, either in value or in the uses for which they are employed.

The growing of China grass or ramie in the Philippines has not yet passed the experimental stage. The species mostly experimented with is the China grass, the seed of which is very much easier to secure than that of the other species. Our last year's experiment with China grass demonstrated that the plant can easily be propagated from seed cuttings, or divisions of the root, and that the plants make a rapid growth. But, owing perhaps to excessive rain, the plants exhibited a tendency to branch too much, thus producing a somewhat short fiber. This year the same experiments have been repeated at the La Carlota experiment station from seed obtained from the plants of last year's experiment. The plants are set out closer together this year, and we hope that this, together with the fact that the plants are to some extent acclimated to conditions here, may produce better results.

Last year we endeavored to obtain seed of the tropical species, the real ramie, or rhea, but our efforts were not successful. A few days ago, however, we obtained a few plants of this and other species of the same genus and have set them out at our Singalong experiment station. These plants are not numerous enough for making a thorough experiment with them, and so we have decided to plant them at Singalong, and as soon as they produce seed in sufficient quantities, we will start experiments with this species on the same lines as those made with China grass.

The cultivation of China grass or ramie on a commercial basis can hardly be said to have been successfully carried on anywhere in the world. The fiber is considered valuable for many important uses, textile and otherwise, but up to the present time none of the many machines invented to clean it have proved practicable. If a satisfactory machine has been

invented, then we can safely say that there are good prospects for the cultivation and production of either ramie or China grass in the Philippines. Such a machine will at once change the position of the fiber from secondary to one of primary importance.

The ramie or China grass fiber is strong and durable and possess a great resistance to moisture. It is said to have three times the length of the European hemp. It can be divided into filaments of the fineness of silk. In certain forms of manufacture it can be used as substitute for cotton, wool, or silk, and also in some instances it can be used in connection with those fibers. The only drawback to its use for textile purposes is its lack of elasticity. This fiber can be easily dyed in all shades and colors, and it can be made to have a luster and brilliancy not unlike that of silk. It also produces a very superior kind of paper, the fineness and texture of its pulp rendering it particularly valuable for making bank-note paper.

The present value of this fiber in the London market ranges between 400 and 450 pesos per ton. Unfortunately, its supply is not steady and is far below the demand for it. A larger supply will undoubtedly bring about an increase in the number of uses made of it, and eventually an increase in its value and in the demand for it.

Recent shipments of the fiber out of Hongkong have been made at a price of £44 (\$214) per ton in London, and prices lately have been ranging from \$200 to \$225 gold per ton. Two years ago \$175 gold per ton was considered a good price, and Hongkong exporters declare that there is money in the production of ramie by the Chinese process at as low as \$100 gold per ton. The demand for the fiber is much greater than the supply, and doubtless would be much greater yet if the supply could be made more certain, since a steady supply at rates which could be depended upon in a reasonable way would lead to the more general use of the fiber for purposes for which it is adaptable, but for which it is now seldom employed because of the uncertainty of the supply. Among the uses to which it is now put is the manufacture of gas mantles, for which purpose it is said to be especially suitable.

MANUFACTURE AND PRICES OF GRASS CLOTH.

The second item of native exports from Amoy to the Philippine Islands during the year 1912 was Chinese grass cloth (declared exports \$6,595 gold). The bulk of this grass cloth was made in the Province of Kiangsi and transported overland to Amoy, whence it was shipped direct to the Philippine Islands. Practically all of this cloth is used for the making of clothing, some being left in the native state, a brown color; a part, the better, being bleached to an almost pure white; while some is dyed, blue and black being the chief colors. In Swatow, China (about 90 miles south of Amoy), there is a considerable drawn-work industry using grass cloth, but there is no such industry in this city.

The material of which this cloth is made is a fine ramie, grown largely in the Province of Kiangsi. There is some grown in the northwestern part of the Province of Fukien near the Kiangsi border, and in such localities some cloth is woven. The Kiangsi cloth and ramie are considered to be much better.

The weaving of this cloth is done principally by

women and wholly in a native-made loom which is operated by hand. Some of the cloth is made in the houses of the Chinese—it might be described as a "cottage industry"—and a large quantity, perhaps the greater proportion, is made at "factories," buildings in which the number of looms may be ten and to which the operatives come, but the equipment of such buildings in almost no way resembles the large factories such as the word "factory" stands for in the United States.

The weaving of one piece of cloth 34 yds. long and 17½ ins. wide requires the entire time of one person for seven days, for which she receives approximately 50 cents gold. The thread used in making all grades of grass cloth is largely of the same grade, the difference in value of the various products being created primarily by the excellence of the workmanship exhibited by those who weave. The bleaching and dyeing is done after the cloth is made.

Details of Cost.—The following statement represents the approximate cost (in U. S. currency) of a piece of grass cloth 34 yds. long and 17½ ins. wide (English measure) completed and delivered in Amoy:

4 lbs. (3 catties) selected ramie, at 12½ cents.....	\$0.50
Cost of labor converting 4 lbs. selected ramie stock into ramie thread, at 30 cents.....	1.20
Labor for weaving.....	.40
Profit for weaving house.....	.10
Freight charges, duty, likin, transportation from Kiangsi to Amoy	.65
Agent's profit about 5 per cent.....	.15
	\$3.00

Bleaching and finishing about 3 per cent extra; dyeing and finishing about 2 per cent extra.

The foregoing statement represents the methods in the "factories," but the women who make the grass cloth in their houses prefer to buy the hemp unsorted, paying for the raw material 62 cents for five catties, or 9⅜ cents per pound for 6⅔ lbs. This the women sort, selling the refuse for use in making native rope and obtaining therefrom 25 cents, so that the cost of the 6⅔ lbs. of raw material to them is reduced to 37 cents, or to 5½ cents per pound.

Complicated Marketing System.—It will be noted that a considerable portion of the cost of the cloth in Amoy is made up of duties and transportation charges. The method of production and marketing of this cloth will explain these apparent high costs. In order to assemble the products of the various places where the cloth is made, collectors go from house to house and from village to village collecting and buying the bolts of cloth. Having collected about 100 bolts, they then sell them to a buyer of the class that might operate a "factory." These, in turn, sell them to the buyers who come from the coast cities or the larger interior cities which either have a market for the grass cloth abroad or who can sell a great deal of the cloth in the cities in which the weaving of grass cloth is not an industry. The coast buyer, or perhaps the large collector in the interior, then arranges for the transportation of the grass cloth from the interior to the larger or distant cities. As there are no railroads and no

highways, all the transportation is effected either by pack animals or the rivers. The larger part of the journey from Kiangsi to Amoy would have to be by pack animals.

The wholesale price of the grass cloth is determined by the buyers mentioned, the cloth being sold by them to middlemen and by the latter to local shops by classes, each class consisting of 20 bolts. For instance, Nos. 1 and 2 of the samples forwarded might be included as different grades of the same class. Each lot of 100 pieces (or bolts) would cost about \$300 (gold), but the classes will be divided so that one group of 20 may be worth \$75 and another less than \$60. Sales of less than 100 bolts would be considered as a middle ground between wholesale and retail, the latter being understood as selling directly to the consumer.

The value of the individual bolts is determined by the quality of the weaving as well as the grade of ramie used. Again, the value of the bolt depends upon the general uniformity of the weaving of that particular individual bolt, some being woven very uniformly at the beginning while near the end of the same piece the weaving may be much inferior. As all the weaving is hand labor, it is impossible to have the same degree of uniformity as is possible with machinery.

Retail and Export Prices.—The price of the cloth to the consumer varies considerably, as there is no one standard either as to cloth or price. When the cloth has come into the hands of the local shop dealer, he then subdivides the groups of 20, placing the higher prices upon those bolts or rolls which are made of the finer cloth and are woven with the greater care. It is plain that the ultimate price to the consumer depends largely upon the last seller. It is equally plain that there are many possibilities for making varying degrees of profits between the manufacturers and the final consumers. The finer grades of bleached cloth (sample No. 3) sell for between 3½ and 9 cents gold per foot (8 to 20 cents Mexican per Chinese foot of 14.1 ins.). Samples Nos. 1 and 2 sell between 3¾ and 5 cents gold per foot (8 to 12 cents Mexican per Chinese foot of 14.1 ins.).

All the samples forwarded are made in Kiangsi and from Kiangsi hemp. The low average export prices per bolt for 1913 are given in gold as follows. (It is to be understood that these prices fluctuate each year with supply and demand):

Sample No. 1—34 yds. by 17½ ins. (English measure). Lots of 100 bolts, \$3.40 per bolt; lots of less than 100 bolts, \$3.60 per bolt.

Sample No. 2—34 yds. by 17½ ins. (English measure). Lots of 100 bolts, \$3.20 per bolt; lots of less than 100 bolts, \$3.40 per bolt.

Sample No. 3—23 yds. by 15¾ ins. (English measure). Lots of 100 bolts, \$2.25 per bolt; lots of less than 100 bolts, \$2.50 per bolt.

Before the importation of cheaper grades of foreign cottons, clothing made of grass cloth was extensively

worn in the summer time by the middle and upper middle classes, but with the importations of foreign cottons the use of grass cloth has declined.

CUBAN RAMIE FIBER.

Ramie is now being produced in Cuba, and this consulate general is forwarding samples of bleached and unbleached Cuban ramie fiber [which have been sent to the United States Department of Agriculture]. A machine has recently been perfected by Mr. Eduardo Mejer of Habana for decorticating this fiber, and the samples forwarded represent the work of this machine. The Compañía Cubana de Fibras Sucesor Eduardo Mejer has been formed to grow ramie on a large scale and decorticate and export the fiber. Shipments have already been made to Germany, and it is stated that the product is so satisfactory that the company has received orders for many tons of the fiber.

It is claimed by the company that ramie plants reach a sufficient growth for making satisfactory fiber in two months during the summer season when the rains in Cuba are abundant, so that it is possible to raise three crops during the period from April to November. There is not sufficient rain during the winter months to grow the plant.

RAMIE IN THE ROVE.

A ramie-spinning concern at Kirkstall, near Leeds, which is making a success of the manufacture of this fiber, informs us that they are now able to spin yarns which are spoken of in the very best terms in regard to strength, roundness, evenness, luster, good wearing qualities, etc. Some counts which they spin on the metric scale they can afford to sell rather cheaper than the corresponding counts of linen yarn on the flax scale, and their quotations for the yarns generally are no higher than those asked in the linen trade for superior linen yarns.

The question has often been asked by Ulster and other flax spinners, who can see their way to utilize the fiber profitably, how they must proceed to spin it successfully. The fact that the above-named company is now putting ramie on cardboard tubes in the form of "rove," from which any flax spinner can easily spin on his ordinary line machinery, will be interesting news for them and for manufacturers. The latter, by weaving it mixed with flax, may thus produce goods more suitable for various special purposes than if they were woven from linen only—in respect, for example, of lightness, strength, non-rotting qualities, etc. The ramie-spinning works referred to understand thoroughly how to degum ramie, and are experts in its preparing for spinning and weaving. Flax spinners and manufacturers (weavers), having the material placed thus at their disposal, should accordingly be able to make use of ramie without depressing the linen industry. On the contrary, the demand for linen yarn should be increased by its being utilized in place of other high-priced textiles, and by the demand which would arise for different descriptions of goods now unobtainable.

Strength of Ramie.—Dr. J. Merritt Matthews, head of the chemical and dyeing department of the Philadelphia Textile School, in his book, "The Textile Fibers" (published by Chapman & Hall, Ltd.), London, in 1907, states that the torsional resistance of hemp is 95, of flax 80, of silk 600 and of cotton 400, if ramie be taken as 100. The following table gives the chief physical factors of the ramie fiber in comparison with the other principal fibers:

	Ramie.	Hemp.	Flax.	Silk.	Cotton.
Tension	100	36	25	13	12
Elasticity	100	75	66	400	100
Torsion	100	95	80	600	400

It will be observed from this that Dr. Matthews considers there is no doubt whatever that the torsional resistance to strain possessed by ramie is really 100, which is 5 more than that possessed by hemp, and 20 more than that possessed by flax, though it is inferior to that of silk and cotton.

[Ramie fiber is admitted into the United States free of duty. It nearly all comes from China, some of it via Hamburg, whence 650,000 lbs. were shipped to American firms in 1912.]

PULVERIZED COAL IN MALLEABLE PLANT.*

Recent discussion in Pittsburgh district as to the possibilities in pulverized coal, both in boiler practice and in metallurgical furnaces, has led to frequent inquiry by large consumers of fuel as to possible costs in boiler and metal-melting operations. The interest displayed in the subject in the past two years, particularly with the pressure of the Smoke Inspection Department of the city of Pittsburgh for better smoke conditions, led the Knox Pressed & Welded Steel Co., of Pittsburgh, controlling the Walker system for burning pulverized coal, to prepare a series of bulletins, dealing with the utilization of the pulverized coal process in boiler installations and metallurgical plants.

These bulletins quote from a series of most illuminating tests made at Erie, Pa. Though the tests in question were made several years ago, they were conducted under private supervision, and the results were not made public at the time.

These bulletins call attention to the known fact that, with average conditions existing in a malleable iron foundry, the cost of fuel laid down at the furnace, annealing oven and boiler are generally higher, as a whole, than fuel costs in other industries consuming the same tonnage. This difference can be accounted for from the facts:

1. That furnaces, annealing ovens and power plant are not located in close relation to one another.
2. That a different class of fuel is used for melting purposes than is used for annealing and boiler purposes.
3. That owing to the different classes of fuels used, and the different places they are unloaded and stored,

*From the Industrial World.

it is impossible to install labor-saving appliances without a heavy outlay.

Malleable iron foundries located in natural gas districts are to a great extent exempt from some of the troubles to which the users of bituminous coal are subject, especially where the gas is used for both melting and annealing purposes. Those using fuel oil are put to practically no trouble or expense in connection with the handling of the fuel, but the cost of the product is so great at the present time as to make its universal use practically prohibitive.

The bulletins recall that over 10 years ago a number of malleable iron foundries were depending upon fuel oil as a heating agent in connection with annealing ovens and at that time, and prior, its cost was low enough to put it on a par with the burning of bituminous coal on grates. But shortly thereafter the oil companies announced that fuel oil would be advanced at expiration of contracts. At that time oil could be bought at 1 $\frac{3}{4}$ cts. per gallon.

The Erie Malleable Iron Co. of Erie, Pa., were using fuel oil at that time, the majority of their bookings being on long time contracts on which it was impossible to increase their selling price; hence they found it necessary to resort to some other fuel for annealing purposes. The Knox bulletins tell what happened, in this fashion:

B. J. Walker, treasurer and general manager of the company, had for a long time been under the impression that pulverized coal could be used, and immediately started experimenting, the results obtained being so satisfactory that they completely equipped their annealing ovens and boilers for the burning of same, and were compelled to use only one car load of oil after their contracts expired.

It must not be taken from the above that their task was an easy one, and that they had plain sailing from the start for such was not the case. On the contrary, they had six months of experimenting, in which there were continual disappointments.

Mr. Metcalf, the president, with Mr. Walker and Mr. Hay, their mechanical man, practically camped on the job, denying themselves the ordinary pleasures they were accustomed to, but by perseverance they gradually overcame each problem as it presented itself, and finally had a perfect working system, and have for years been reaping the harvest of their labors, while their competitors have (with one exception) been going along in the same old extravagant way.

Outside of the cement manufacturers, very few understood the value to be derived from the burning of pulverized coal, until a few months back. The sudden interest displayed by nearly everyone in any way connected with metallurgical work was brought about, in the identical way that started the Erie Malleable Iron Works experimenting—namely, the announcement by a large oil company that the price of fuel oil would be raised. Fuel oil up to this time had advanced very little but conditions were such that to continue to use this form of fuel would be ruinous to those engaged in the iron and steel industry and consequently investigators were sent by the large manufacturers broadcast over the country to investigate cheaper methods and results have been that nearly all of the larger manufacturers have, or are contemplating, the installation of pulverized coal in metallurgical furnaces."

There is a reason other than economy that has had a great deal to do with the installation of pulverized coal in certain localities, declares the bulletin. Cities in which a smoke ordinance has been passed, and in

which smoke inspectors are continually on the job harassing those with smoky chimneys have to some extent forced the issues, where it was found that a cheap bituminous coal can be burned, that will be smokeless. Speaking of malleable foundry costs, the bulletin says:

We doubt very much if there is a malleable iron foundry in the country that can show annealing costs as low as, or any-ways near those of the Erie Malleable Iron Company—namely less than 90 cents per ton on annealed castings.

This cost is based upon coal at \$2 per ton f. o. h. foundry, and includes the cost of drying, pulverizing and conveying and all labor in connection therewith, and is an average cost covering five years.

Further, the pulverizing plant furnishes all of their facing, a considerable amount in a foundry of this size.

The annealing ovens in this plant are under continuous fire for 120 hours, and the temperature maintained is from 1,650° to 1,700° F.

Another consideration worthy of note in connection with pulverized coal in annealing ovens in comparison with hand firing of coal, is the steady uniform temperature: the oven is not cooled by the continual opening of doors, and once the desired temperature is reached in the oven it can be held there for hours, without adjusting the controller.

Very excellent results were likewise secured with pulverized coal in connection with boilers in the Erie plant. The Knox bulletin details tests made in 1903 by the students of the engineering class, Sibley College, Cornell University, on one of these boilers to determine the efficiency of the boiler using pulverized coal. The results of this test are the more remarkable, when it is taken into consideration that the boiler tested was one of a battery of six horizontal tubular boilers that had been in constant use for years, and had had no special preparation for the test. The results obtained were as follows:

Duration of test.....	10 hours
Kind of fuel.....	pulverized bituminous
Horsepower developed	129.87
Builders' rated horsepower.....	100.00
Percentage of builders' rated hp. developed.....	129.87%
Evaporation from and at 212° per pound combustible....	10.353
Efficiency of boiler and furnace.....	72.05%

"It is hard to say," concludes the bulletin, "just what results would have been secured had the boiler been of the modern water-tube type, and thoroughly clean and free from scale. However, the above results go to prove the efficiency of pulverized coal. From the data which we have in our possession, and which we know to be authentic, it is reasonable to assert that pulverized coal costing \$2 per ton is equal to fuel oil at one cent per gallon, and natural gas at eight cents per 1,000 feet. A large saving can also be shown over hand and stoker firing of coal, and the best gas producer practice.

"Pulverized coal has been used very little in connection with reverberatory furnaces in malleable iron foundries, but there is absolutely no reason why it should not be, as it is very successfully used in open-hearth furnaces, the coal required to melt a ton of metal being below 500 pounds, in furnaces of 30-ton capacity.

METALLURGY.

ON THE DETERMINATION OF TITANIUM AS PHOSPHATE.*

By GEORGE S. JAMIESON and RICHARD WREN-SHALL.

Several years ago Eric John Ericson¹ described a method for the determination of titanium in ferro-titanium and in ores. The method was based upon the precipitation of titanium phosphate in acid solution by the addition of ammonium phosphate and boiling, after reducing the iron to the ferrous state by means of ammonium bisulphite or sulphur dioxide. He gave the factor 0.336 for calculating the titanium from the weight of the phosphate, assuming that the latter has the formula $Ti_2P_2O_8$.

On account of the simplicity and rapidity of this method its accuracy and application have been studied in this laboratory. Some modifications of the original method have been found desirable and its application to the separation of titanic acid from alumina has been worked out. A series of 18 experiments was made with standard solutions of ferric and titanic sulphates containing enough sulphuric acid to keep the salts in solution, but the quantities of free sulphuric acid present were not determined.

The standard titanium solutions employed in this research were prepared from pure potassium titanium fluoride with the exception of one solution made from a titanium oxalate of excellent quality. The titanium salts were converted into the sulphate by repeated evaporation with sulphuric acid in platinum dishes. The solutions were standardized by precipitating the titanium with ammonia from measured volumes, finally weighing the dioxide and calculating the strength of the solution in terms of titanium. The values obtained were checked by precipitating the titanium by the sodium thiosulphate method and weighing the dioxide.

In each case 15 cc. of 1:1 hydrochloric acid were added to measured volumes of these solutions, water was added to make the volume 100 cc., sulphur dioxide was passed through for 10 minutes, the liquid was heated to boiling and 20 cc. of a 10 per cent solution of ammonium phosphate were added. The boiling was continued for a half hour; the precipitate was allowed to settle for an hour or more; it was then filtered and washed with hot water on a Gooch crucible in which it was finally ignited for 15 minutes at the highest temperature of the Bunsen burner and weighed. The method of Ericson was closely fol-

lower here except that the Gooch crucible was used instead of paper for filtering, on account of the tendency of the precipitate to run through a paper filter. In order to make satisfactory use of the Gooch crucible, it is necessary to use moderate suction and to avoid allowing all the liquid to pass out of the crucible until thorough washing has been effected, for it is impossible to wash the precipitate after it has become compact and has cracked. Except with very small quantities of titanium, the results obtained were satisfactory. Low results were obtained when less than 0.007 gram of titanium was present, which appear to be due to the failure of the precipitate to collect in a filterable form. It probably remains in a colloidal condition. The writers have found that with such small quantities of titanium less acid must be used and after precipitation and boiling, it is advisable to let the liquid stand for at least 6 hours, then to warm on the steam bath and filter. With this treatment the loss appears to be no greater with about 0.002 gram of titanium than with larger quantities.

When an attempt was made to apply Ericson's method to some ores containing 0.5 to 8 per cent of titanium it was found that no precipitate or only a small one was obtained if the ores had been dissolved by treatment with hydrochloric and sulphuric acid and evaporation with a rather large amount of sulphuric acid instead of being dissolved by a potassium bisulphate fusion. This was evidently due to the presence of the large amount of sulphuric acid in addition to the hydrochloric acid used. Therefore, when this convenient method for dissolving titanium ores is employed, it is necessary to neutralize the sulphuric acid, best with ammonia, before proceeding with the determination. Titanium ores or minerals not decomposed by the acid treatment just described, are rendered soluble by fusion with potassium bisulphate in the usual manner.

In the analyses in Table I the sulphuric acid present in each solution was neutralized with ammonia before adding the hydrochloric acid; the precipitates were allowed to settle at least six hours, then the solutions were heated on the steam bath for about 20 minutes before filtering.

In these experiments a volume of about 50 cc. was used instead of 100 cc., as in the case of the first series of experiments. It will be observed that in the first ten experiments very small amounts of titanium were taken in order to determine the conditions under which they could be satisfactorily precipitated and filtered. It is evident from these experiments that when 1-3 mg. of titanium are present, it is necessary to keep the amount of free 1:1 hydrochloric acid down

*From The Journal of Industrial and Engineering Chemistry.

¹Iron Age, Aug. 27, 1903, p. 4.

to about 3 cc. in 50 cc. solutions, otherwise low results will be obtained.

Experiments were made to find if titanium phosphate could be precipitated in the presence of tartaric acid and it was found that this could be done quantitatively although in a recent article Thornton² states that titanium cannot be precipitated by any reagent in the presence of tartaric acid. To the solutions containing measured quantities of titanium and ferric sulphates, about 2 grams of tartaric acid were added and enough ammonia to make them slightly alkaline. Then hydrogen sulphide was passed into the warm solutions until the iron was reduced and precipitated as sulphide. The solutions were treated with 10-15 cc. of 1:1 hydrochloric acid, depending upon the amount of iron present, and heated until the iron

procedure was as follows: To 0.5 gram of very finely pulverized sample, 25 cc. of concentrated hydrochloric acid were added and the solution was heated upon the steam bath until no further action was observed. About 20 cc. of 1:2 sulphuric acid were added and the solution was cautiously evaporated to sulphuric acid fumes and then heated for an hour at a temperature just below the boiling point. After cooling, 30 cc. of water were added and the solution was warmed until the soluble salts had dissolved. The insoluble matter was filtered, washed three times with very dilute sulphuric acid, and finally with water at room temperature. The insoluble matter was tested and was found to be free from titanium. The filtrate was diluted to exactly 500 cc., mixed thoroughly, and aliquot parts were taken so that the ignited precipitate would not weigh over 90 mg., as it was not practical to attempt the filtration of larger amounts of this gelatinous precipitate. To each aliquot part 2 grams of tartaric acid were added and the method from this point was identical with that described above. Three titanic iron ores were analyzed with the following results:

TABLE I.

No.	Fe taken.	Ti taken.	Ti found.	Error.	Cc. 1:1 HCl used.
1.....	0.000	0.0019	0.0018	-0.0001	1
2.....	0.000	0.0030	0.0027	-0.0003	3
3.....	0.000	0.0030	0.0034	+0.0004	3
4.....	0.043	0.0010	0.0010	±0.0000	2
5.....	0.086	0.0010	0.0009	-0.0001	3
6.....	0.086	0.0030	0.0029	-0.0001	3
7.....	0.086	0.0010	0.0009	-0.0001	3
8.....	0.086	0.0019	0.0011	-0.0008	6
9.....	0.086	0.0010	0.0002	-0.0008	6
10.....	0.086	0.0039	0.0032	-0.0007	10
11.....	0.043	0.0100	0.0101	+0.0001	5
12.....	0.043	0.0154	0.0152	-0.0002	5
13.....	0.043	0.0154	0.0151	-0.0003	5
14.....	0.100	0.0248	0.0245	-0.0003	15
15.....	0.100	0.0248	0.0244	-0.0004	15
16.....	0.100	0.0260	0.0256	-0.0004	15
17.....	0.110	0.0260	0.0258	-0.0002	15

sulphide was dissolved. Then 20 cc. of the 10 per cent ammonium phosphate reagent were added and the experiments from this point were identical with those described above. In the first four experiments the ferrous sulphide was filtered off and washed with hot water containing a little ammonium sulphide, while in the last four the ferrous sulphide was not filtered, but dissolved as previously directed. No advantage was gained by removing the iron from the solution. The following results were obtained:

No.	Fe taken.	Ti taken.	Ti found.	Error.
1.....	0.086	0.0207	0.0206	-0.0001
2.....	0.043	0.0050	0.0049	-0.0001
3.....	0.043	0.0030	0.0024	-0.0006
4.....	0.043	0.0040	0.0039	-0.0001
5.....	0.013	0.0060	0.0059	-0.0001
6.....	0.200	0.0249	0.0253	+0.0004
7.....	0.100	0.0186	0.0186	±0.0000
8.....	0.100	0.0249	0.0248	-0.0001

The choice of methods for the reduction of the iron is largely a matter of personal preference, since both give equally good results as seen in the tables of test analyses given above. However, it may be said that the reduction of the iron in our ammoniacal solution is somewhat quicker than that by sulphur dioxide in a hydrochloric acid solution.

In applying this method to the determination of titanium in some ores, which were previously found to be completely decomposed by acid treatment, the

Ore.	Ti found.	Ti by the volumetric method ³ .
A.....	13.00%	13.18%
A.....	13.17	
A.....	13.20	
B.....	24.19	
B.....	23.99	24.22
B.....	24.22	
C.....	15.82	
C.....	15.86	15.94
C.....	16.01	

It is recommended that for the general application of this method to the determination of titanium in the presence of relatively large amounts of iron, the titanium be precipitated from a solution of about 100 cc. volume which contains 15 cc. of 1:1 hydrochloric acid. Furthermore, it is recommended that enough substance be taken so that at least 10 mg. of titanium shall be present in the solution.

It was found that titanium could be separated from aluminium and determined in the same manner as when iron is present, but that it was necessary to use more hydrochloric acid in order to prevent the pre-

TABLE II.

No.	AlO taken.	Ti taken.	Ti found.	Error.	Cc. conc. HCl used.
1.....	0.063	0.0273	0.0277	+0.0004	10
2.....	0.060	0.0310	0.0308	-0.0002	12
3.....	0.070	0.0248	0.0245	-0.0003	10
4.....	0.063	0.0248	0.0249	+0.0001	9
5.....	0.110	0.0210	0.0214	+0.0004	10
6.....	0.100	0.0260	0.0263	+0.0003	11
7.....	0.120	0.0310	0.0309	-0.0001	14
8.....	0.060	0.0223	0.0224	+0.0001	15
9.....	0.060	0.0186	0.0189	+0.0003	8
10.....	0.050	0.0186	0.0182	-0.0004	15
11.....	0.070	0.0248	0.0245	-0.0003	10
12.....	0.060	0.0122	0.0119	-0.0003	7
13.....	0.050	0.0248	0.0292	+0.0044	5
14.....	0.100	0.0310	0.0473	+0.0163	5
15.....	0.150	0.0186	0.0233	+0.0047	7
16.....	0.100	0.0248	0.0288	+0.0040	5
17.....	0.070	0.0310	0.0351	+0.0041	7

³A modification of the method in Gooch's "Methods in Chemical Analysis," page 242.

²Am. J. Sci., 34, 214.

cipitation of aluminium phosphate. The method employed was to add 1-2 grams of tartaric acid to the solution of titanium and aluminium sulphates and enough ammonia to make it slightly alkaline. (The tartaric acid was used to prevent the formation of the hydroxide.) Then a measured quantity of hydrochloric acid was added and the analysis was completed in the same way as when iron was present. A volume of about 100 cc. was used in the experiments shown.

These experiments indicate that with a volume of 100 cc. containing 0.05-0.15 gram alumina it is necessary to have an excess of at least 8 cc. of concentrated hydrochloric acid in order to get a satisfactory separation of the titanium.

LOW CARBON PIG IRON FOR IRON CASTINGS.*

An important contribution to the metallurgy of cast iron appeared in *Stahl und Eisen*, November 27, 1913, in an article by Alexander Zenzen on "The Application of Additions to the Charge in Producing High Value Cast Iron." A large portion of it follows:

In scientifically managed foundries it has been known for some years that the strength of cast iron depends not only on its chemical composition but also essentially on its structure; that a good cast iron, on which the severest demands as regards strength and density can be made, must have a structure of fine grain. This can be attained with certainty only by melting iron in a crucible, because there is no essential change in the original definite mixture due to the absorption of foreign ingredients. The best crucible cast iron is characterized by a low carbon content, which is not more than 3 per cent. In a cupola it is difficult to produce a good cast iron with less than 3 per cent carbon because the cupola charge of pig iron seldom has less than 3 per cent carbon and because also carbon is absorbed from the coke. The addition of steel scrap to produce higher tensile strength, though somewhat in favor, has also similar disadvantages arising from the use of coke, from the absorption of sulphur, etc., so that real success is never attained in this way.

USE OF ENGLISH BRANDS IN GERMANY.

A few grades of cold blast charcoal pig iron, such as the English brands Frodair, Coldair, etc., have found special favor in Germany as an addition to cast iron to bring about a dense iron. They serve in many foundries, despite their high cost, as a cure-all without which dependable results are impossible. The analyses of these irons, recognized as especially valuable English brands, are by no means entirely good, especially as regards sulphur, manganese and phosphorus. The feature which confers on them the valuable property of producing a cast iron of very fine structure combined with density and strength is their low total carbon content.

In his capacity as managing engineer of a large

Rhineland metallurgical plant, Alexander Zenzen was active in the iron foundry where iron of quality was made and where large castings with a minimum tensile strength of 18 kg. per sq. mm. were poured. The average thickness of all kinds of castings to be produced varied between 5 and 100 mm., and therefore it was not possible to keep one cupola in operation which could produce the necessary composition for these different transverse sections. Manifestly the strength of cast-iron sections is dependent on the structure; and the structure, in uniform foundry practice and conditions, is dependent on the chemical composition, which, however, cannot be changed so often nor in such short intervals as would be demanded by the thickness of all of the pieces to be poured. In spite of this, it was possible to pour each piece in the grade of iron as to composition corresponding to the transverse sections. Daily 10 to 15 tons of castings were to be poured for which a high tensile strength was demanded. Two small cupolas of 3 to 4 tons capacity produced two grades of cast iron. One cupola, with a charge of No. 3 hematite (1 to 1.5 per cent silicon), steel rails, scrap and Siegerländer alloy, produced a so-called hard iron of the following prescribed composition:

	Per cent.		Per cent.
Carbon	3.00	Phosphorus	0.10
Silicon	1.00	Sulphur	0.10
Manganese	0.50	Copper	0.10

The other cupola, with a charge of No. 1 and No. 2 hematite, low manganese iron, and scrap, produced a so-called soft iron of the following composition:

	Per cent.		Per cent.
Carbon	3.50	Phosphorus	0.10
Silicon	2.50	Sulphur	0.07
Manganese	0.05	Copper	0.10

To pour castings with a thickness of less than 10 mm. the straight soft iron was used; for those of 10 to 15 mm. thickness, a mixture of $\frac{2}{3}$ soft iron and $\frac{1}{3}$ hard iron; for those of 20 to 25 mm., $\frac{1}{2}$ hard iron and $\frac{1}{2}$ soft iron; for castings of 30 to 40 mm. thickness, $\frac{2}{3}$ hard iron and $\frac{1}{3}$ soft iron, and for castings of greater thickness only the hard iron was used.

The hard iron of the cupola was blown with tolerable certainty of a constant quality because the ingredients of the charge had a constant composition. Nevertheless the superintendent had a sample taken of every tap of the cupola, making the hard iron by taking a test with a spoon from the partly filled ladle after quickly stirring it. When the test piece, poured in sand and cooled in water, showed the expected amount of separation of graphite, the partly filled ladle was then at once filled with the amount of iron from the soft iron cupola necessary to make the mixture desired. This resulting mixture was then properly stirred with a rod of iron fastened to a piece of rail after a piece of lead had been thrown into the ladle. In this manner the volatilization of the lead as well as the stirring gave the gases a chance to

*From *The Iron Age*.

escape. Each day a test piece one meter long and 30 mm. thick was taken of the hard iron, the soft iron and the resulting mixtures, and tested for bending and other properties.

EXACTING CONDITIONS MET.

Manifestly in this manner it was possible to produce every desired mixture, and therefore any casting of a definite weight and limited cross-section. The most exacting demands as to density of structure and as to tensile strength and resistance to pressure could thus be satisfied. The results were decidedly satisfactory. No modifications were possible, and all chemical calculations for soft iron, hard iron and the finished product were the result fundamentally of the silicon content. A chemical laboratory was available and always open for use. Tensile strength tests of the products were taken almost daily. From the numerous tensile tests and also especially the bending and pressure tests, in conjunction with the chemical analyses, Mr. Zenzes became convinced that in the case of two test pieces of similar chemical composition as regards Si, Mn, P, S, and Cu, an essential difference in tensile and pressure characteristics could ensue. The literature on the subject, as well as all previous practical experience, could offer no solution of this phenomenon. It was manifest, however, from the square test pieces used to determine the resistance to pressure, that of two pieces of like chemical composition as regards Si, Mn, P, S, and Cu, but of entirely different strength, the hardness of the pieces poured in dry sand differed in degree. From this the conclusion was drawn that the carbon content was the real measure of the physical properties of cast iron.

BEST RESULTS WITH CARBON UNDER THREE PER CENT.

The analyses for total and combined carbon afforded fully the right explanation: that of two test pieces of similar structure and chemical composition as regards Si, Mn, S, P, and Cu, the tensile strength is greater the less the percentage of total carbon and the higher the combined carbon in a test piece of gray structure. In the best cast iron with gray structure the percentage of combined carbon was from 0.80 to 1.00; of graphitic carbon about 2 per cent; and the total carbon not over 3 per cent. Investigation of the cupola iron showed that the carbon content of the hard iron was mostly under 3 per cent, and therefore there resulted the best breaking tests with a tensile strength of 28 to 30 kg. per sq. mm. from a total carbon of not more than 3 per cent and often less.

The desire arose, therefore, to produce a cast iron with less than 3 per cent carbon. Attempts to do this in a cupola direct were unsuccessful because no pig iron with less than 3 per cent carbon was available and because melting pure cast iron or steel scrap with ferrosilicon produces an iron of poor quality. Entirely different results are obtained when the white iron, blown at a high temperature in a converter, is used to mix with pig iron. By this means a desired or cal-

culated composition results and always a carbon content of less than 3 per cent attained. These experiments Mr. Zenzes announced in his patent, "Process of Producing Cast Iron of High Tensile Strength." This process is used with great success in numberless plants having small Bessemer converters.

MAKING LOW CARBON PIG IRON.

In 1904 Henning, in Mannheim, announced a process for making a pig iron that will produce dense castings; it consists of mixing liquid pig iron and liquid steel. It is a German patent (D. R. P. 179,739). In using this process a converter outfit is unnecessary. Two German blast furnaces are operating very successfully in accordance with this process of Henning's, which enables blast furnaces to make a pig iron low in carbon. The English special irons, which have increasingly entrenched themselves in many German and foreign iron foundries, are being displaced by this iron from the two blast furnaces.

The success attending the use of briquettes of borings in foundries rests principally on the lowering of the carbon content. The use of special pig iron of low carbon content to produce castings of dense structure and high tensile strength appears to be better practice.

BENEFICIAL EFFECT ON MAGNETIC PROPERTIES.

Of special importance is the use of special pig iron to produce castings which shall possess special magnetic properties. A cast iron has the best magnetic properties which has a low carbon content of fine-grained and dense structure. The combined carbon, of all other ingredients, has a lessening effect on the induction and should not be higher than 3 per cent. The lower the percentage of combined carbon, the lower is naturally the total carbon, provided that the elements which aid in the formation of combined carbon, such as manganese, sulphur, etc., are present in corresponding amounts. A silicon percentage of 2 to 2.50 is best because it hinders the formation of combined carbon and furthers the separation of graphite.

The experiments of Mr. Zenzes which led up to his patent, referred to before, showed that his product had excellent magnetic properties. The complaints of the electric industry that it is difficult to obtain cast iron of satisfactory electric permeability come to an end if castings are produced according to the process of Mr. Zenzes. It is true that by the use of steel scrap in the charge success has been attained in producing an iron having improved magnetic properties, but the use of low carbon pig iron is to be preferred under all circumstances.

Gratification is expressed that due to scientific efforts German founders are free from foreign fetters, being in a position to replace the special English irons with their own low carbon grades. Castings poured at the Concordiahütte from these irons carry conviction from their appearance, as to their wonderfully dense and uniform structure.

SMELTING OF ORES AND METALS.*

With the view of developing more efficient methods in the smelting of ores, the bureau began at its Pittsburgh experiment station a detailed investigation of the practicability of using the electric furnace as a substitute for or adjunct of the blast furnace, with particular reference to the treatment of low-grade ores.

One problem studied is the possibility of using crude oil as a reducing agent. The result of these experiments, which were made by J. F. Cullen under the direction of D. A. Lyon, were incorporated in a report for publication. Another problem, still under investigation, is the possibility of using the electric furnace in the smelting of copper ores, especially sulphides. The experiments incidental to this investigation included work on:

1. The smelting of copper concentrates. Experiments have been made to determine to what degree loss of copper in the slag could be lessened by smelting these concentrates in an electric furnace.

2. The use of the electric furnace in the smelting of nonferrous ores. The purpose of this investigation is to determine the feasibility of using electricity as a source of heat in smelting copper-iron sulphide ores, lean zinc and lead ores, and in fact all low-grade ores that are not amenable to treatment by wet methods, and especially to ascertain whether the electric furnace may be used profitably for treating ores from deposits that are so far from a smelter that transportation charges exceed the value of the metals in the ores. In some cases it may be possible to use hydroelectric power in an electric furnace, thus removing the necessity of transporting worthless gangue, and enabling the metals of the ores to be transported as matte or crude metal, providing it was not feasible to refine the metal at the smelting plant.

3. The use of the electric furnace as an aid to the ordinary blast furnace. In the study of this problem the following points have been considered:

- (a) The possibility of recovering the iron in the slag as metallic iron. At present, as is well known, although the iron content of a gold, silver, copper, or lead ore may be large, it goes to the dump in the slag, either as iron oxide or iron silicate.

- (b) The possibility of producing ferro-silicon from the slags ordinarily obtained in smelting nonferrous ores.

- (c) The recovery of the sulphur as a by-product in the smelting of sulphide ores.

- (d) The discovery, if possible, of some suitable collector or carrier other than copper and lead for the precious metals in smelting practice.

The purpose of the work has not been to show that the electric furnace should replace reverberatory or

the blast furnaces, but that in some places it may be substituted for them. So far, only the possibility of treating copper sulphide ores has been studied. The results of the work will be published in a bulletin. The electric furnace work for these investigations has been done by R. M. Keeney, under the direction of D. A. Lyon.

New investigations proposed for the coming year include: The electric smelting of zinc ores; the smelting of titaniferous iron ores; the production of "natural alloys"—that is, the production from complex ores of alloys containing different metals in such proportions as to be of commercial use for structural materials, for tool making, etc.; the use of an electric process for removing moisture from the blast supplied to blast furnaces; the removal of sulphur from producer gas for metallurgical purposes.

The following reports have been, or are being, prepared for publication:

"The Use of the Electric Furnace in the Manufacture of Iron and Steel," by D. A. Lyon and R. M. Keeney; "The Use of Crude Oil as a Reducing Agent in the Reduction of Iron Ores," by D. A. Lyon and J. F. Cullen; "Smelting of Fine Michigan Copper Concentrates in the Electric Furnace," by R. M. Keeney; "The Use of the Electric Furnace in Metallurgy," by D. A. Lyon, R. M. Keeney, and J. F. Cullen; "The Possibility of Smelting Copper Ores in the Electric Furnace," by D. A. Lyon and R. M. Keeney.

These investigations have been carried on by D. A. Lyon, metallurgist, and J. F. Cullen, Electrometallurgist; W. A. Mueller, chemist (from October, 1912, to January, 1913); R. M. Keeney, Electrometallurgist (from Feb. 1, 1913).

SMELTER FUMES AND GASES.

The following extracts from the third annual report of the National Bureau of Mines, Joseph A. Holmes, Director, gives an idea of the activity of the Bureau during the past year in regard to investigations of smelter fumes and gases:

As during the previous year, the investigations conducted at the San Francisco experiment station and the field work controlled from there, have centered around the problems of copper and lead smelting, with especial reference to the reduction of the deleterious gases and fumes emitted by smelting furnaces, and the recovery of the valuable constituents, now wasted, of these fumes.

Considerable time has been spent in attempts to find new uses and to encourage the extension of present uses of sulphur, arsenic, bismuth, selenium, and tellurium, which are found in such amounts in these wastes that if any large proportion of the whole

*From the forthcoming third annual report of the National Bureau of Mines, Joseph A. Holmes, Director.

were collected in commercial form the supply would exceed the present demand.

During the year the laboratory work has been largely devoted to the quantitative study of the fundamental chemical reactions taking place in roasting and blast furnaces, in the converter, and in other standard smelting equipment.

A large part of current operating practice is based on empirical generalizations that have gradually been developed in the art itself. Although practice must, of course, always be the court of final resort as regards the merits of a given procedure, still there are many fundamental chemical problems on which more definite and accurate quantitative data are badly needed, and which can not be advantageously studied in industrial furnaces. These are receiving especial attention in the laboratory. At the same time the attempt is being made to render the field investigations and the work in co-operation with industrial plants throughout the country serve as a medium for carrying the theoretical conclusions and suggestions from the laboratory to a point where they may be readily interpreted into practical improvements and methods of closer control by those in charge of smelters.

A significant and encouraging fact is the cordial co-operation in this work which has been extended from the industries concerned, even in those cases where the work in question dealt with bettering the condition of the workman or of the surrounding community without immediate prospect of commercial advantage to the operating company.

This co-operation has in many instances been wholly informal consisting merely of the exchange of suggestions or of especial facilities for making certain tests. In other instances it has taken a more definite form, as in connection with the Anaconda and the Selby smelter commission. Both the Anaconda plant in Montana and the Selby plant in California has been in litigation either with farmers' associations of the local or the Federal Government over alleged fume damage for many years, and much time and money had been expended in court proceedings by both sides without apparently reaching any permanent settlement of the general questions at issue.

The court proceedings in both these cases have within the last two years been suspended, and by agreement the questions of fact have been referred to commissions of disinterested experts for investigation and report as to what improvements are possible and practicable and what relief may be reasonably expected. While these commissions are entirely independent of the Bureau of Mines as an organization, the director of the bureau was asked to serve on each of them as an individual, and, with the approval of the Secretary of the Interior, is so doing.

Each of these commissions has its own staff of

scientific and technical investigators, but the bureau is assisting the broader aspects of their investigations, in the attempt to make such of the results as do not involve confidential data available for the broad general study of these problems.

The work of the San Francisco station has been under the general direction of F. G. Cottrell, chief physical chemist, with a staff consisting of L. H. Dushak, chemical engineer (from Jan. 9, 1913); V. H. Welch, assistant physical chemist (furloughed Jan. 16, 1913, and since then in the employ of the Anaconda commission); W. Eaton, assistant physical chemist (resigned Sept. 6, 1912); D. R. Kellogg, assistant physical chemist (from Jan. 2, 1913); and E. H. Zeitfuchs, mechanic and laboratory assistant.

PETROLEUM INVESTIGATIONS.*

The bureau's investigations relating to the efficient production and utilization of petroleum and petroleum products includes the study of well-drilling methods, with especial reference to the prevention of waste of oil and gas at wells on or adjacent to public lands; the study of methods of storing and transporting oil and natural gas with a view to lessening loss in transit and in storage; the study of means of decreasing fires from lightning, which have caused heavy losses in the southern and middle western states; the study of refining methods in order to ascertain the best process of refining petroleum and improving the quality and increasing the yield of commercial products; and the study of fuel oils belonging to or intended for the Government, with especial reference to increasing efficiency and economy in their utilization.

Investigations of methods of drilling wells, and the various types of drilling rigs, tools, and appliances were continued in California, Oklahoma, Louisiana, Colorado and Wyoming, and in other States. Methods used in the Oklahoma oil fields were studied in detail, and samples of oil were obtained from all the producing fields of the State.

In November, 1912, Ralph Arnold, petroleum engineer, visited the California oil fields in company with J. A. Pollard, consulting engineer, with the object of investigating methods of preventing the waste of oil and natural gas from flowing wells. Especial attention was given to the capping of gushers and gassers in the "gusher territory" of the Midway-Sunset fields. In December Mr. Arnold conducted a similar investigation in company with Mr. A. C. Mortenson, and in January made an extended trip in company with W. R. Calvert, consulting geologist, to investigate the prevention of waste and the most efficient methods of utilizing oil and gas in connection with "topping" and natural-gas gasoline plants.

*From the Third Annual Report of the National Bureau of Mines, Joseph A. Holmes, Director.

The results of some of these investigations were published in a technical paper, and a description of the cementing process of excluding water from oil wells as practiced in California was published as another technical paper.

In the latter part of the fiscal year a study of the different methods used at oil wells in California for recovering oil was made, and the results were prepared for publication.

The bureau has made a careful examination of the conditions attending the development of oil and gas pools in Oklahoma, many of which are in Indian lands, in the endeavor to ascertain the wastes of oil and gas under the existing methods of drilling wells and of transporting and utilizing gas and oil, and to discover means whereby such waste could be prevented without hardship to the operator and to the advantage of the public.

To ascertain the conditions that have led to enormous waste of natural gas in Kansas and Oklahoma, L. S. Blatchley, consulting geologist, visited the principal oil pools in those States. He found that not only had little effort been made to save gas (casing-head and flow-tank gas) at many oil wells, but that gas wells had been allowed to blow into the air daily millions of cubic feet of this ideal natural fuel. He also found that there had been great waste in the utilization of gas, chiefly through using it for purposes for which it should not be used, or selling it at prices that discouraged economy in its use. Mr. Blatchley also found that there had been much waste of petroleum in the form of sludge and residue from oil tanks. His findings are being prepared for publication as a technical paper.

As a result of its investigations in California and Oklahoma the bureau ascertained the feasibility of drilling oil wells in Oklahoma by means of cable tools and the use of mud-laden water to plaster the sides of the wells, and thus prevent the escape of gas from sands overlying the oil sand. Having ascertained the practicability of the method, the bureau had one of its petroleum engineers, J. M. Pollard, demonstrate the ease with which wells could be drilled and waste of oil and gas prevented when the method was used. Already the waste of millions of feet of gas has been stopped and the life of the Cushing gas field has been prolonged. Further work will probably demonstrate the value of the gas in this field, and pipe-line connections may then be made to transport the gas to a market.

Already the methods introduced in the Cushing field are being used in the field near Okmulgee, Okla. These methods not only save gas, prevent water from entering gas or oil sands, and decrease the liability of disastrous fires, but enable wells to be completed at less cost than by the methods hitherto used in that State.

THE REORGANIZATION OF BUREAU OF CHEMISTRY.

With the object of unifying the work of the inspectors and the laboratories under the Food and Drugs Act, the United States has been divided into three inspection districts, the Western District, the Central District, and the Eastern District, each of which will be in charge of a chief of the district, who will have immediate supervision of the work of both the inspectors and laboratories in his district. Heretofore the inspectors and the laboratories worked independently of each other, the inspectors reporting directly to the Chief Inspector at Washington, and the laboratories reporting to the Chief Chemist. In this way the headquarters at Washington was the only co-operating link between the inspection service and the Food and Drugs investigating laboratories.

Under the new plan both the inspectors and laboratories will be directly under a single district chief, and this will bring about absolute correlation in work and complete co-operation between the inspectors and laboratories, and will greatly expedite the handling of samples, holding of hearings, and the preliminary disposition of cases. The chief of the district may send samples taken by inspectors directly to any of his laboratories for analysis, or if his own laboratories do not provide facilities, he may send them to Washington. The chief of each district must send full reports on analyses, hearings and all other matters to the Chief Chemist, and his findings are subject to review at Washington.

The district chief, however, cannot institute a prosecution or a seizure, as all cases calling for prosecution or seizure must be first passed upon in Washington.

The dividing line between the Western and Central districts runs south on the State lines following the eastern boundary of Montana, including the whole of Colorado in the Western district, and the whole of Texas in the Central district.

The dividing line between the Eastern and Central districts runs along the western boundary of Pennsylvania and West Virginia, and follows state lines southward including Georgia and Florida in the Eastern district.

The Western district includes the laboratories at San Francisco, Seattle, Denver, and Honolulu. The Central district includes the laboratories at Chicago, St. Paul, St. Louis, Cincinnati, and New Orleans. The Eastern district includes the laboratories at Washington, New York, Boston, Philadelphia, Buffalo, Savannah and San Juan, P. R.

The Board of Food and Drugs Inspection was discontinued on Feb. 1. The work heretofore done by this Board will be done by the Chief Chemist, who will, when necessary, consult with the specialists in the various laboratories.

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HARRY McCORMACK, Editor.

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NOTES AND COMMENTS.

Peat in Canada.

The experimental work conducted by the Canadian Government in regard to the manufacture of peat, according to a report of the U. S. Consul at Kingston, Ont., proved so successful that there are now two private concerns producing peat, one at Alfred, Ontario, and the other at Farnham, Quebec. It is said that the peat manufactured by the Canadian Government and used by private persons is satisfactory for grates and also good for cooking.

The Government commission which was sent to various European peat-using countries reported that the most successful way to treat the peat was to let the sun and wind evaporate the moisture. After the Government had shown the practicability of producing a good quality of peat at a salable price it was left to private enterprise to continue the work. The peat is sold in Ottawa at \$5 a ton or \$3 a ton on the cars at Alfred.

The Canadian Government in connection with the peat industry will experiment in the production of gas and electrical energy from peat. At the fuel-testing plant in Toronto the Government has a 60-horsepower gas-producer engine that is operated from the peat. Should the present experiments be successful, sections of the central peat-producing districts of Canada where water power is not available will be able to ob-

tain power from a series of these gas-producer engines.

The Origin of a Borax Mineral.

It is generally recognized that boric acid in considerable quantities is an original constituent in the waters and gases given off with volcanic emanations. In fact, the Tuscan fumaroles, in Italy, have been an important commercial source of boric acid for a long time, and in the past, possibly even to the present time, almost all the boric acid brought into the European market has been derived from this source. There is abundant evidence of the presence of boric acid in volcanic emanations in many parts of the world. On the other hand, boron is so rare a constituent of rock-forming minerals that it forms an almost inappreciable small percentage of the earth's rock mass as a whole.

A short study of the borate deposits in Ventura County, Cal., supplemented by more cursory examinations of similar deposits in the vicinity of Death Valley, has been made by Hoyt S. Gale, of the United States Geological Survey, and a new theory of the origin of the deposits of colemanite, or borate of lime, in these regions has been advanced by Mr. Gale in Professional Paper 85, Part A, recently published by the Survey. While this theory has not yet been entirely proved, there is much in its favor and it affords suggestions and a working basis for further observation.

The supposition of a desiccated saline lake to explain the origin of the colemanite has little to support it beyond rather general assumptions. The character of the deposits themselves indicates rather a vein type of formation. Other salines which would naturally be expected in desiccation deposits resulting from natural saline solutions are not found in association with the colemanite. Those who have supported the desiccation theory have offered no explanation of the cause which might produce colemanite in such massive deposits as a product of water evaporation, while, on the contrary, its formation from limestone in veins by replacement of carbonic acid with boric acid is a natural hypothesis that deserves further investigation. The relations of the deposits to basalt lava flows indicate the probable origin of the boric acid at the time of the extrusion of these lavas, although it may be assumed that this acid continued to find its way into solution of the circulating ground waters long after the period of the extrusions.

New Publications of the Bureau of Mines.

The new publications of the Bureau of Mines under List 26—February, 1914, are as follows:

Bulletin 58. Fuel-briquetting Investigations, July, 1904, to July, 1912, by C. L. Wright. 1913. 277 pp., 21 pls., 3 figs.

Bulletin 60. Hydraulic Mine Filling; Its Use in the Pennsylvania Anthracite Fields; a Preliminary Report, by Charles Enzian. 1913. 78 pp., 9 pls., 11 figs.

Technical Paper 39. The Inflammable Gases in Mine Air, by G. A. Burrell and F. M. Seibert. 1913. 24 pp., 2 figs.

Technical Paper 58. The Action of Acid Mine Water on the Insulation of Electrical Conductors; a Preliminary Report, by H. H. Clark and L. C. Ilsey. 1913. 26 pp., 1 fig.

Technical Paper 61. Metal-mine Accidents in the United States During the Calendar Year 1912, Compiled by A. H. Fay. 1913. 78 pp., 1 fig.

Technical Paper 66. Mud-laden Fluid Applied to Well Drilling, by J. M. Pollard and A. G. Heggem. 1914. 78 pp., 12 figs.

The Bureau of Mines has copies of these publications for free distribution, but can not give more than one copy of the same bulletin to one person. Requests for all papers can not be granted without satisfactory reason. In asking for publications, please order them, by number and title. Applications should be addressed to the Director of the Bureau of Mines, Washington, D. C.

6th Semi-Annual Meeting of American Institute of Chemical Engineers.

Announcement has been made that the 6th semi-annual meeting of the American Institute of Chemical Engineers will be held at Troy, N. Y., June 17th to 20th, 1914. John C. Olsen, Polytechnic Institute, Brooklyn, N. Y., is Secretary.

The Bleached Flour Decision.

The Supreme Court of the United States late in February handed down a decision which may exert a marked influence on the national food and drug laws. The decision was made in the case brought by the Government against those millers who bleach flour by an electric method involving the production of the various oxides of nitrogen. Commenting on this the Oil, Paint and Drug Reporter says:

The contention of the millers was that the quantity of nitrite absorbed by the flour was too minute to exert a deleterious effect, but the trial judge in the lower court in his charge, failed to give the jury that part of sub-division five of section seven of the act, in which it is specified that to condemn a food it must contain added poison or deleterious substances, "which may render the product injurious to health."

On the omission of the clause given above between quotation marks, the case was appealed and the Supreme Court has ruled that this qualifying clause should not have been omitted and, therefore the case has been sent back to the lower court for a new trial.

In itself the case would seem of slight interest to the drug trade, but for the fact, that it may foreshadow similar decisions on the benzoate and sulphite questions. But of still greater significance is the decision in affecting the present enforcement of the food and drugs law, since as long as the qualifying phrase given above holds, the Government will have to prove that the deleterious ingredient is injurious to health.

Of course, this opens up the ever-debatable—since

practically non-solvable—question, "What is a poison?" and if the Government had the right to definitely rule that certain ingredients should not be added to food, the enforcement of the law would be simplified.

Perhaps there would arise the danger of arbitrary and unjust use of this power on the part of Government officials. In the very case in question it is a mooted question as to whether a minute quantity of nitrites in flour is really deleterious; whether the presence of traces of that chemical should be prohibited.

Again recent experiments upon animals have shown that continued administration of tartrates produces kidney disease, yet should we prohibit the use of cream of tartar baking powders for this reason?

However, mooted questions are just the ones behind which the unscrupulous love to take refuge, and no law can be efficiently enforced if it contains loop holes similar to the above qualifying clause.

On the other hand the honest manufacturer should know what is demanded of him, and a bureau regulation clearly stating whether a certain ingredient may or may not be used is much better than long drawn-out litigation.

The Supreme Court decision clears the situation inasmuch as it points out in what way the Government is limited in the enforcement of the law. We can scarcely credit the newspaper statements that Dr. H. W. Wiley has declared that the decision "has killed the food and drugs act," since it is plain that the decision is based only on one section of the law, and that regarding phases of enforcement over which there are honest differences of opinion.

We do agree with him, however, in the desirability of eliminating from the statute, the qualifying phrase "which may render such article injurious to health," thus giving the Government freer hand in the formulation of definite regulations. We say this since we believe that such power would be used only for the more efficient enforcement of the statute and since we are equally sure that arbitrary rulings will be quickly reversed, either by the higher officials or by the courts.

Standards for Naval Stores.

The proposal to establish interstate commerce in naval stores on a basis of Federal standardization and authority, has attracted widespread attention throughout the industry. The work of carrying out the plans and purposes of the movement, states the Oil, Paint and Drug Reporter, has been delegated to a committee representing producers, factors, primary buyers, consumers and naval stores inspectors, apparently comprising every practical phase of the industry. Legislation embodying the fundamental features, such as uniformity in grading, weighing, gauging, quality and trading methods, is naturally the most effective medium through which the best results are to be realized, but before any measure can be prepared for reasonable consideration the committee is confronted with the preparation of such a detailed and comprehensive

foundation as to insure harmonious relationship between the different interests, and to encourage the most cordial spirit of support and co-operation in the fulfillment of such legislation as may be adopted.

There can be no question that the methods now in effect for reducing trading in naval stores to a basis that might be capable of specific and tangible association between the various operators have been more or less crude and indeterminate, and frequently, so far as consumers were concerned, it has been a case of Hobson's choice. In the formal statement representing the views of producers and dealers at the Washington conference for the proposed regulation of the industry, it will be noted that particular attention is given to the subject of rosins and this is explained by the fact the present system of grading rosins is especially loose and open to such easy practices of substitution and tampering that the consumer might find his purchase far from his reckoning and purpose. Branding or cutting in the barrel the specific designation the rosin is expected to bear when it reaches the ultimate buyer has been recommended as the most dependable method to supersede the present plan of marking, by which an I grade can readily be raised to K, or an E standard easily changed to F. Color and freedom from dirt and foreign matter are the only practical tests upon which the grading of rosins is to be determined. The color basis, it would seem, should be settled most satisfactorily by the adoption of color glasses conforming as nearly as possible to the existing types as well as to the long-established trade customs, but insuring a reasonable safeguard against the irregularity and insecurity prevalent under the practices now in effect. The determination of a basis of cleanliness is apparently within practical reach and a suggestion has been made in the local trade that any default from a recognized standard of cleanliness could be penalized by a lowering of the product's general grading standard.

Supplementing the report of the conference between the officials of the Department of Agriculture and the representatives of the naval stores industry, as published in last week's issue of the Reporter, our Washington correspondent gives further details of the proposed standardization and legislation which appears in the current number. First reference will be to the present and suggested types for rosin. Ten grades are chosen as a basis for showing the average color intensity according to long established trade custom. From these types have been evolved proposed color gradings for standard recognition, which present no material variances from the general average of present tests, but have the advantage of specific and tangible determination. An objection has been raised to the adoption of glass colors as an official basis for grading rosins as involving an outlay of \$75 per set, which expense might be burdensome to the small producers.

So far as establishing a standard for turpentine is

concerned, the color test alone seems to have been under consideration as the means of working out a tentative basis. The Bureau of Chemistry has taken the 1914 types of the Savannah and New York markets, showing a wide latitude in the different specifications, New York representing the higher standard. The proposed official basis is more or less of a compromise between the two market types, and as affecting the color question is seemingly within reasonable and practical limits of uniformity at minimum specifications of 150 millimeters for "white," 50 millimeters for standard, 25 millimeters for "one shade" and 15 millimeters for "two shades." There will be urged on behalf of some of the trade interests that the standardization of turpentine be based on other than mere color test so as to establish a higher recognition of merit and fulfillment of consuming requirements. Petroleum distillates have been chiefly employed as adulterants of turpentine in the various distributing centers, and it is claimed that the color standard alone would be inadequate to check this evil. Specific gravity, distillation and polymerization tests have been suggested as additional means of safeguarding the interests of buyers in general and of consumers in particular. A number of the states have adopted laws against the adulteration of turpentine without fixing any established basis upon which purity is to be determined. The Navy Department specifications afford probably the most stringent standard. As amended December 24, 1912, it imposes in addition to the general characteristics, the requirements of specific gravity, refractive index, boiling point, distillation, polymerization and color tests.

The establishment of standards for naval stores is a subject with which the Department of Agriculture is well qualified to cope, supported by the practical assistance of trade representation, but there are questions of particular trade significance, such as weights, tares, etc., for the consideration and solution of which there has been suggested the organization of a national naval stores association to include producers, factors, primary buyers, exporters and consumers. The advantages of regulating the production and marketing of naval stores redound positively to consuming interests and it is urged that they should have a larger representation on the committee empowered with the plans for the proposed legislation. We believe that the subject is one to command the early attention and consideration of the various paint, oil and varnish clubs of the country.

Essential Oils in Hongkong.

Exports of various essential oils of South China and Indo-China production to the United States and Europe, according to the U. S. Consul at Hongkong, are developing into a trade of considerable volume and value. The chief oils of this sort are aniseed and cassia oil, but there are other varieties of oil which have value and are being exported. Various oils are

produced for Chinese use which are usually too expensive for foreign markets at present prices, but which are likely to have value in exports in the near future.

The production and export of cassia oil has increased materially during the past year. Exports to the United States, however, decreased in value from \$76,682 in 1912 to \$67,696, in 1913, but shipments to Europe increased by about 50 per cent. There was an increase in exports of star aniseed oil, the value of shipments to the United States having increased from \$92,138 to \$93,199. According to the returns of the Hongkong Chamber of Commerce, shipments of essential oil generally to Great Britain increased from 437 cases in 1912 to 777 cases in 1913, while shipments of these oils to the continent of Europe increased from 4,304 cases in 1912 to 6,567 cases in 1913.

During the past year there were great fluctuations in the price of both of these oils as a result of speculation. The price of the highest grade of cassia oil ranged from \$200 local currency, or \$101 gold, per picul of 133 $\frac{1}{3}$ pounds in January, 1913, to as high as \$205 local currency, or \$104 gold, in April, and then gradually fell to as low as \$176 in November, and closed the year at \$178, or \$86.25 gold, per picul at current exchange. Cassia oil comes in three grades, the lowest ranging from 70° to 75° test, the next at from 75° to 80°, and the best at 80° to 85° test. The price of aniseed oil followed a line similar to that of cassia oil during the year, ranging from \$390 local currency, or \$197 gold, per picul in January, to \$410 local currency, or \$200 gold, per picul in May, and closing the year at \$335 local currency, or \$164.15 gold, its lowest price for the season. Aniseed oil comes in one grade only. The chief center of production of each oil for the Hongkong market is in the Province of Kwangsi.

Among other oils produced in Hongkong territory for export or for sale to the Chinese is peppermint oil. The Chinese product is almost colorless, with pleasant peppermint odor, and resembles in composition mentholized peppermint oil imported to Europe and the United States, largely from Japan. It is reported as having some qualities superior to the Japanese product, but usually runs somewhat higher in price in the redistilled form. This oil, as made by the Chinese, is quoted in local markets at present as worth from \$130 to \$230 local currency, per picul of 133 $\frac{1}{3}$ pounds—from about 47 cents to \$1.08 gold per pound. Peppermint crystals also are exported in considerable quantities, present quotations being around \$2,200 local currency, per picul, or about \$7.75 gold per pound.

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COLLOIDS.*

Colloid chemistry is a relatively new field of chemistry and physics, although many of the facts of the subjects, notably the discoveries of Graham, have been of record for a considerable time. It is difficult, however, to give a concise definition of a colloid. There are no general considerations which permit us to tell what are, or what are not, colloids. One must apply a series of tests—a sort of qualitative colloid analysis. Methods have been found, as a matter of fact, that enable us to put almost all classes of substances into the colloidal condition.

The conception of colloids originates from diffusion experiments. Graham, who first investigated quantitatively diffusion phenomena, found that while many substances migrated rapidly, others such as glue, gelatin, silicic acid, tannin, aluminum hydroxide, the gums, and albumins migrated very slowly, if at all. He attempted to distinguish between the two groups by methods other than this simple diffusion experiment. In this connection he designed the gelatin jelly test. Above a 2 per cent gelatin jelly in a test tube he placed the solutions, and he observed the rates of diffusion downward into the jelly. He further modified this test by putting a parchment membrane or other animal tissue between the two layers. He found that those substances that diffused rapidly went through the membrane, while those that did not diffuse were held back. This is the phenomenon of dialysis. Graham here made the first generalization; the diffusing substances he called crystalloids, the non-diffusing substances he called colloids. He defined a colloid, then, as something in solution which did not diffuse, and did not dialyze.

But this definition is not sufficient. Are colloids coarse precipitates, or are they molecular solutions? This point was never settled. Modern colloid chemistry believes it better to consider what is common to all classes. There is no sharp line of demarcation between them; they are all transitions. There is a continuous series of conditions and phenomena. Let us call the whole group "dispersoids,"—a system in which the properties change continuously. And we will divide this group into three sub-groups, which division, however, is entirely arbitrary. It has been found

practical to use $.1 \mu$ (approximately the limit of microscopic visibility) to distinguish between precipitates and colloids. This limit has been chosen because suspensions of particles of diameter $.1 \mu$ are stable, and do not settle. The pores of fine filter paper are 1μ in diameter, so one can use filtering as a rough test. The upper limit of the "degree of dispersion" of colloids is approximately the molecular diameter. We have selected as the upper limit $1 \mu\mu$. This then is the answer of colloid chemistry to the question, What is a colloid? It is a dispersed system in which the particles range in diameter from 100 to $1 \mu\mu$. We may distinguish colloids from solutions by their lack of diffusion, and by dialysis. We may distinguish them from fine precipitates by the filtering test. Also colloids are very stable in the absence of electrolytes. But there is perfect continuity throughout; our demarcations are purely arbitrary.

Since the size of the particle seems to be the important distinguishing characteristic, one would conclude that any substance in the proper degree of dispersion would be a colloid. Quite empirically, experience has shown that this is correct. We have colloids of many numbers and kinds.

There are two methods of making colloids: (a), starting with molecular solutions and letting them grow—the condensation method; and (b), starting with solids and dividing—the dispersion method. Thus we can get colloidal gold by reducing gold chloride with phenyl hydrazine to get blue gold, or with tannin to get red gold. On the other hand we can apply the dispersion method and obtain colloidal tungsten by grinding up the metal mechanically; by the action of light on a gold plate; or by the action of the electric current between metallic electrodes under water. In the condensation method it seems that the size of the particles is a function of the concentration of the molecular solution we start with. This function shows a maximum corresponding to a definite concentration. Thus with very dilute and with very concentrated solutions, the size of the resulting particles is very small.

Until recently only liquids were considered as colloidal solutions. But we see that if it is true that a particular degree of dispersion is the defining condition of a colloid, we ought to have colloids that are not liquids. We should have cases of a solid in a gas,

*From a series of Five Lectures delivered by Dr. Wolfgang Ostwald at the University of Chicago.

of a solid in another solid, of a solid in a liquid, of a liquid in a liquid (emulsion), of a gas in a liquid (whipped cream, beer foam). Notice in each case we have a dispersing medium which dissolves the other material. Alloys and cast iron are instances of solids in solids; in cast iron is found ferrite, graphite, and carbides of iron. We have also the solid solutions of Van't Hoff. Glass can assume a red color due to colloidal gold dispersed in the solid medium, our common ruby glass. In a gaseous medium gold dispersed as the solid as in smoke, also shows the red color; in fact gold everywhere can give this color. In the mineral kingdom these systems also are common. Water may be held in crystals as droplets (coarse), as ultra-microscopic particles, or held as water of crystallization, the molecular solution. Then we have the case of clouds—a liquid in another gas. The cosmic dusts likewise show very different degrees of dispersion. Only in the case of a gas dissolved in another gas, does this conception of colloid not apply. Thus, this general conception enables us to take into consideration an enormously larger number of systems, most of which science has not yet investigated. Thus the subject of foams, fumes, fogs, smokes, all colloidal from this point of view, have hardly been opened up, as yet.

Let us consider from the scientific point of view, this special degree of dispersion. Let us consider first, the variation in physical properties with variation in the degree of dispersion. If we examine some particles of carmine under the microscope, we find that they are in continuous motion. If we exclude all influencing conditions, we find that they still move. In fact such suspensions in minerals can be seen which have been in motion for thousands of years. This is called Brownian movement. All kinds of dispersoids show this motion, if the viscosity of the medium is small enough. And the velocity of the motion is greater with increasing smallness of the particles. When we study the nature and cause of these motions, we go into the field of the Kinetic theory. We conclude that these motions are the kinetic movements already assumed for gases.

The diffusing property ought to depend upon the size of the particular substance. Thus Pictet and Lume, working under Ramsay, showed all transitions of diffusion. Taking arsenic trisulphide, and varying the concentration, they obtained a series of precipitates from coarse, which settle quickly, through finer and finer, to real molecular dispersion. The stages may be represented as follows: (1) settle quickly—coarse; (2) settle same day—microscopic, partly retained on filter; (3) pass filter, invisible under microscope, non-dialyzable; (4) finest precipitate—partially dialyzable; (5) typical colloid, mostly dialyzable; (6) solution—molecular dispersion. Filter paper pores range in size from 3.3μ to 1.3μ . Colloids have a diameter of $.1 \mu$. Colloids diffuse through jellies as through water. Highly dispersed colloids go through jellies no matter how fine, if pressure is applied. Very

concentrate jellies, such as the copper ferrocyanide semi-permeable membrane, will hold back certain molecules. Thus by this method of ultra-filtration we may fractionate colloidal particles of different sizes.

Next we may consider turbidity. There is the perfectly clear colloidal ferric hydroxide and the visibly turbid colloidal sulphur. There are perfectly clear colloids. But there are methods to detect very small traces of turbidity ordinarily invisible. This is the sun dust phenomenon, or the Tyndall effect. If we make similar conditions under the objective of the microscope so that we look at right angles to the beam of light, we see little spots of light. We do not see a definite picture as from a reflection process, but only little sources of light which come from diffraction phenomena. The same results can be obtained by ultra microscopic methods against a dark background, as in the case of a mastic suspension in water. If we investigate molecular dispersion, we find the same result. Extreme instances are sugar and sodium sulphate. In concentrate solutions, these show exactly the same kind of Tyndall cone. We are not astonished that salt solutions, liquid ether, organic liquids in general, show ultra violet cones when examined through quartz dishes. Tyndall cones are thus seen in diluted salt solutions and in systems like ether; thus there are all degrees of optical dispersion.

Next consider color. Colorless dispersoids show merely opalescence, against a dark background appearing blue, against a light background appearing yellow. Thus we would expect that colloids might have all colors, which is actually the case. Gold may be red, blue, orange, green; silver may also be any, in fact nearly every color. Color is mainly due to the size of the particles. The finest have a yellow to orange color, larger and larger particles go through changes in this order; red, violet, blue and green, the latter being the coarsest. In the case of gold we are not to think of the color of its plane surface but its color by transmitted light. Faraday found the color of thin gold to be green, corresponding to fairly coarse particles. The blue particles are smaller, violet yet smaller, then though red to orange, the first being the color of the most highly dispersed condition possible. The color of a gold solution with a colorless anion is brown or orange. Silver shows the same changes. It is blue in thin sheets. Its solutions are faintly yellow. The smaller the size of the particles, the less the color of the liquid. At the highest dispersion silver salts are practically colorless.

What happens when an electric current is passed through these three kinds of dispersoids? There is conduction—a transport of substance. The ions are the material carriers. They may be charged positively or negatively, or with zero charges, in which latter case the particles move very slowly. The sign of the electric charge is not necessarily constant for any given material.

We can change the sign by additions of other mate-

rials or by changing the medium. Silver iodide shows both kinds, depending upon which kind of ion is in excess. By pouring a solution of potassium iodide into one of silver nitrate the colloid is produced positively charged. By pouring the silver nitrate into the potassium iodide the colloid becomes negatively charged. The migration of colloids can be shown very neatly by the aid of filter paper. Filter papers are suspended above dishes of colloids with the bottom edge of the paper dipping into the respective solutions. The colloids climb up the paper, or not, with the liquid according to their sign. Cellulose always assumes a negative charge when dipped into water (in fact, if large quantities are used sparks may be produced). Positively charged colloids are precipitated and do not rise in the cellulose, while negatively charged colloids climb with the fluid. It is not to be thought that the amount of colloid material moved by the current is proportional to the chemical equivalents. The phenomenon is rather similar to conduction in gases. Here likewise the path of the migrating ion can be changed by magnetic influences. This is known as the Hall effect. Thus we see that the physical properties of the three groups of dispersoids change steadily and progressively.

The chemical properties are fully as important. Do they change continuously or not? In the case of solubility the following result was noted: Hulett found that finely powdered gypsum is about a hundred and twenty times more soluble than crystalline gypsum. This does not refer to the rate of solution, but to the final or absolute solubility. The catalytic effects, represented by the decomposition of hydrogen peroxide by platinum black, depend upon the size of the particles. Colloidal platinum in exceedingly small amount decomposes the peroxide. Such effects are produced by "specific surface," that is, the amount of surface in units volume. The increase of surface with decreasing size of particle is a startling and commonly unknown quantity. Consider the following table:

Edge of cube.	Number of cubes.	Total surface.
1 cm.	1	6 cm. ²
.1 cm.	10 ³	60 "
.01 cm.	10 ⁶	600 "
.001 cm. (diam. of blood corpuscle = .0007 cm.)	10 ⁹	6,000 "
1 u (.0001 cm. = diam of small coccus)	10 ¹²	6 sq. m.
.1 u	10 ¹⁵	60 " "
.01 u (limit of ultramicroscopic visibility)	10 ¹⁸	600 " "
.001 u or 1 uu	10 ²¹	6,000 " "
.1 uu (diam. molecules)	10 ²⁴	60,000 " "

A platinum plate does not decompose peroxide; a coarse dispersoid does the act better; colloidal platinum does it best of all; solutions not at all.

There are two different kinds of colloids, represented on the one hand by colloidal gold, silver, platinum, etc., on the other by antimony trisulphide, gelatin, silicic acid, aluminum hydroxide, etc. The physical characteristics of the two groups are quite different. In not too concentrated form the colloids of

the first class have practically the same viscosity as water. The viscosity of the second class varies from 0 to infinity (taking water as zero). The viscosity of the colloids of the first class is directly proportional to their concentration. The members of the second class show a sudden break in their viscosity-concentration curves. This is the "setting" point or critical point. This difference must necessarily indicate a change or difference in the aggregation of the molecule. This is explained by the affinity of one of the classes for water. Thus there are two grand divisions of colloids—Suspensoids (lyophobic—not liking liquids and Emulsoids (lyophilic—liking liquids). The emulsoids, therefore, have incorporated in them a certain quantity of water in combination. The critical point, it should be said, may be displaced or entirely eliminated by the addition of electrolytes or non-electrolytes.

It is further noted that gelatin solutions and emulsoids in water, in general, secrete a liquid. This secreted liquid is a dilute colloid. Its amount depends upon the acid or electrolyte content, etc. This is syneresis.

Emulsoids absorb liquids. This is shown by the swelling of rubber in benzol, and the swelling of gelatin in moist air. When a silver chromate precipitate is formed in a gelatin medium, instead of a continuous layer being formed, the precipitation takes place intermittently in the form of concentric circles.

When water is secreted from the colloid, it may coagulate. This can be brought about by mixing two colloids of opposite electrical charges, or by shaking, so that air particles become intimately mixed with the colloids. The higher in valence the colloid is, the quicker and easier the coagulation is effected. By the same process two colloids may absorb each other. Usually you obtain in this manner a particle which must be at least the size of two colloids. Under these conditions a precipitate is formed, and the reaction is quantitative.

APPLICATIONS OF COLLOID CHEMISTRY.

(a) To Other Sciences.

The methods used to prevent the passing of fine precipitates (colloids) through filter-paper in analyses are adaptations of the principles of colloid chemistry. The precipitated material may be allowed to stand so that small particles may grow into larger ones; the solution may be boiled to get coagulation of the suspensoids; or the solution may be shaken with salts. The use of color reactions of metal colloids such as gold colloid, to show presence of small amounts of metal, is another application. The intensity of the colloid color often is greater than that of aniline dyes. This permits of detection of very small traces of the metals. In the case of gold, a borax "pearl" will show the presence of .002 millionths of a milligram, while the spectroscope will show but .12 millionths of a milligram. The sensitiveness of the colloidal and spectroscopic silver tests is in the same ratio. The

color reactions of metal colloids may be widely applied. Natural money gives a yellow silver colloid, which the artificial does not give. There is an essential oil in the natural product which is the reducing agent, and which has not yet been introduced into the artificial product. Humic acid can be detected in peat by the use of the gold test.

In photography, it has been assumed that the latent image is due to reduction of the silver halide to subhalides (three in number, to account for the varieties of colors obtained in developing). It is now found that the substance is composed of silver halide with metallic silver in the colloidal state. The different colors result from the different degrees of dispersions of the colloid. Red, green, blue, brown colors can be obtained if colloid silver is added in different amounts. The products appear as colored crystals. Hence crystallization does not always mean that we get a pure substance.

Many compounds are absorption substances. All the slippery, slimy, gluey substances which will not crystallize, which have no sharp melting or boiling point, show the typical properties of colloids. A special kind of dispersoid is the system isoprene-India rubber. In the process of polymerization we see the isoprene get viscous. At first the polymerization product can be dissolved out with absolute alcohol. Afterwards it gets more and more like rubber, and is a colloid. The first phase is a mixture of iso-colloids or iso-dispersoids. Plastic sulphur exists in two allotropic modifications likewise. So with the iso-colloids, as isoprene goes over to rubber. These are sometimes called allo-colloids.

Many of the organic dyes are colloids and this certainly affects their properties. For example, the sulphur dyes show color changes as functions of temperature. If metal colloids may change color this way, the idea is justified that the dye color changes may be due to changes in their colloidal state.

Many crystals are colloidal, as shown by the ultra-microscope.

Colloids obey the same law of density (La Place) as the air. In this way the number of molecules in one gram of gas can be calculated and so Avogadro's law proved.

Cosmic dust is supposed to play a large part in the origin of worlds. Movement of the dust by light pressure is the first step in this evolution; and is influenced by the size of the particles. The greatest speed is with particles 10 to 100 μ in diameter. These are typical colloid dimensions.

Many minerals are representative types of colloids. For example, while ordinary rock salt is colorless, a blue variety is known. The blue color is due to the presence of colloidal sodium, produced probably by the radio active influence of potassium compounds.

There is a series of silica minerals of practically the same composition, except for water—pure quartz, chalcedony, opal, etc. This whole series of minerals

parallels a series of dispersoids of greater or less degree of dispersion. Quartz is supposed to be insoluble in KOH; chalcedony is easily soluble. If, however, quartz is very finely ground, so as to get greater degree of dispersion, KOH dissolves it. Silica dissolves to the extent of 1.6% under ordinary conditions, but if ground to pass a 5 μ sieve, 10% will dissolve.

Soil is a conglomeration of colloids of varying degree of dispersion. Soil physics is colloid chemistry.

A very large application of colloid chemistry is made in the biological sciences and in medicine. Human beings consist mostly of colloids. Protoplasm and albumins likewise are such. Living cells show the Brownian movements. When cells are killed coagulation occurs. Histology deals with colloid chemistry. Water absorption accounts for many of the phenomena of cell history. Likewise muscle movement may be explained on the colloid basis. The colloid metals are used in therapeutics. Colloidal silver in the space of silver nitrate is used in the eyes. Colloidal sulphur is used in skin diseases, colloidal calomel in syphilis, colloidal gold in cancer, and the very latest is colloidal paladous hydroxide in obesity treatment.

(b) *To Industries.*

Colloids are quite generally distributed. For example, wood wool, silk cotton, the dyes (indigo and the blacks), leather (tanning), soap (washing), coffee—all are colloids. Two dyes may be chemically identical, yet have entirely different hues. Two clays, chemically the same, so far as analysis can tell, make entirely different bricks. It is only natural, considering the newness of colloid conception, that many applications at present consist merely in the recognition that colloids exist in the particular instance. Colloid chemistry is young and in many branches this first step of recognition is the only one made. Real scientific application is just beginning.

Many observations have been made, however, since ancient times. In the manufacture of soap, salting out and coagulation have been practiced for many ages. In India rubber, which shows the baffling cases of vulcanization, one of the first steps is probably absorption. Acheson working with graphite found that increasing the degree of dispersion until the colloidal state is reached, increases the lubricating properties to a most remarkable extent. An important problem in this connection was to find a way to protect the colloid against precipitation by electrolytes. Acheson, following the biblical method of the Egyptians who used a decoction of straw in the manufacture of bricks, used tannin as a protecting material. The explanation is that the emulsoid forms a film about the colloid, keeping each particle shielded from foreign influence. Ruby glass, many precious stones, and ultra-marine are colloids.

The behavior of the hydraulic substances such as mortars, cements, etc., have been explained on the basis of a "hydraulic" theory. This theory offers no

explanation of shrinking, elasticity, or hardness. All these properties can be explained on a colloid basis, and the ultra microscope substantiates this. In the manufacture of clay pottery, colloidal aluminum hydroxide plays a very important part. To this is due the property of plasticity. How to gain this plasticity for moulding and yet have less water to dry out afterwards is a new art. The material may be made so thin as to be cast, all the while having less water than the stiff clays which may be cut with a knife. Some of the finest china is cast this way. The viscosity of the paste is decreased enormously by the addition of a small amount of alkali. At one particular concentration of the alkali we get a permanent suspension of the clay. Greater or smaller concentrations do not serve. This phenomenon of increasing the degree of dispersion is called peptonization.

A most important and interesting application is in metallurgy. In the carbon-iron series of alloys we have a typical colloid system; the degree of dispersion changes from coarse, in pig iron, where we have the big microscopic crystals, through the finer grades as in common, annealed, and carbon steels, to the molecular dispersion of the solid solutions. All grades of austenite are so called solid solutions in the iron; martensite is a molecular solution of carbon in iron; pearlite is a more coarse suspension of carbide in iron. Characteristic structures which come between the two extremes, which are neither one nor the other, are osmondite and sorbite; they are peculiar to the tempered steels and show maxima of properties; the dispersion is just that of colloidal size. In the making of the best steels, therefore, the aim is to make colloids.

There are industries which we must call colloid industries, because they have been so from the beginning, and handle only colloids. The cellulose industries are of this sort—paper-making, the manufacture of parchment paper, mercerizing cotton, and the manufacture of artificial silk.

All the processes used to make celluloid, and plastic masses like bakelite, and those processes starting with casein, are colloid industries. Celluloid is a solid solution, containing camphor; bakelite is an isocolloid, a polymerization of phenol and formaldehyde with alkali. Other colloid industries are the India rubber industry, which in both the coagulation and vulcanization processes presents a fertile field for the application of colloid ideas; also the manufacture of starch and glue. In the sugar industry, the problem is to obtain all the sugar from the molasses. Cooking processes are largely colloidal, not only in the case of jellies, jams and gelatins but in other operations such as the cooking of steak where the problem is to form a coagulated layer over the outside quickly to retain the juices. The ageing of bread is another instance of syneresis. The precipitation of solids from

smoke and dust by the famous Cottrell process is a typical colloid reaction.

If one asks how it is that there can be a brand new science of such a wide application, how it is that only recently the colloid idea has appeared as of universal extent and supreme importance, the answer is that science in general has occupied itself with two big classes of materials. Matter has been studied either in bulk or in molecular solution. Very much has been learned about these two conditions, at the same time neglecting a whole world of dimensions in between. Because we can conceive of converting everything into these dimensions it is to be expected that the new science will have such a wide applicability.

METAL MINING INDUSTRIES IN WESTERN STATES.

During the past several years development in the metal-mining industries of the Western States, according to the third annual report of the National Bureau of Mines, Joseph A. Holmes, director, has fallen far short of that of agriculture. In some of these states there has been a decline rather than an advance in mining development. Thus, in the states of Colorado, Idaho, and Montana—the only states for which we have such records—the average number of men employed in the metal-mining industries for the five years ended December 31, 1912, is but 69 per cent of the average number of men employed during the five years ended December 31, 1907. The total number of men in those industries in these three states was 61,107 in 1900, and only 28,461 in 1912.

During this time, furthermore, there has been little advance in the annual values of mineral products. Meanwhile, however, agriculture in these Western States has had the advantage of an agricultural experiment station and an agricultural school established and maintained by the Federal Government in each state; and it has also had the advantage of the expenditure of approximately \$92,000,000 since 1902 in the irrigation and development of large areas of public lands in each state.

As a means of carrying forward the needed investigations looking to the upbuilding of the mining industry in the public-land states, it will be highly advantageous either that a considerable number of mining experiment stations be established in those states, or that additional funds be provided to enable the Bureau of Mines to conduct such general investigations in those states as is believed will aid in a better development of the metal-mining industries of the country.

A bill introduced into the Ontario (Canada) legislature by the Minister of Lands, Forests and Mines, provides for a reward of \$25,000 to the first person who discovers radium in the Province in sufficient quantity for commercial extraction.

NOTES ON THE SEWAGE DISPOSAL PLANTS OF GLASGOW AND LONDON.*

By KENNETH ALLEN.

There are three excellent chemical precipitation plants at Glasgow which clarify the sewage before its discharge to the Clyde. From the lower two, at Dalmuir and Shieldhall, the sludge is taken by steamers 39 miles below the Dalmuir works to a point off Garock Head, where it is discharged through mushroom valves in the bottom of the ship. It takes about 25 minutes to load the Dalmuir steamer with 960 long tons of sludge each day, delivered through two 16-inch gravity pipes from elevated sludge tanks of a capacity of 3,000 tons. The steamer itself was freshly painted and scrupulously clean and there was no offensive odor, at least above deck, to suggest the use to which it was put.

The river here is lined for miles with the busy ship-yards for which Glasgow is famed. At the time of my visit the rival of the Imperator, the Aquitania, had been recently launched in the presence, I was told, of over 100,000 persons. Its extreme length had made it necessary to excavate a very considerable amount of material from the bank of the river opposite the ways to prevent damage to the vessel or obstruction to navigation. This gives a conception of the width of the Clyde as compared with some of our American rivers, as well as of the great size of the ship.

The third plant lies above the center of the city at Dalmarnock, and as the river is not navigable for large vessels here the sludge is pressed and, in part, further dried to eighteen per cent moisture, screened and ground in a pug mill for use as a fertilizer. The demand for this at from 12s to 20s per ton is only sufficient to dispose of the product during three months of the year. The other three months the crude sludge cake is sold to local farmers.

The authorities evidently feel that the time is approaching when the effluent from these works lying above the city must receive further treatment before discharge to the Clyde, for I found there a trickling filter covering about one and two-thirds acres in course of construction. This comprises four rectangular beds of broken granite, varying in size from four inches at the bottom, where it rests on four-inch drain tiles, to one and one-half inches, covered with screenings on top. The traveling distributors, manufactured by Ham, Baker & Company, run on rails and are operated by two stationary motors with wire rope transmission, the current being furnished by the municipality.

The following data are for the year 1911-12:

Total sewage.....	30,334.8 million Imp. gals.
Average daily flow.....	82,882,103 Imperial gallons
Total sludge.....	755,142 long tons
Total grit and screenings.....	9,197½ long tons
Crude sludge to presses.....	228,400 long tons
Cake produced.....	42,662 long tons
Cost per ton for pressing.....	1s. 9½d.

Sold as manure.....	42,758 long tons
Sold as "Globe Fertilizer".....	195 long tons

DISPOSAL OF SLUDGE AT SEA.

	Shieldhall	Dalmuir
Sea charges.....	3.3d.	2.2d.
Land charges.....	1.1d.	0.9d.
Average moisture contained.....	87.71%	85.25%
Weight of sludge per million Imperial gallons.....	22t. 5cwt.	23t. 9cwt.

At London the sewage is conveyed by interceptors to two large chemical precipitation plants, one at Barking on the north side of the Thames, and one at Crassness on the south side. Experiments have been carried on at the former within the past couple of years in the omission of chemicals and substituting plain sedimentation. The cost of precipitation with a volume of 118,040 million Imperial gallons in the year 1911-12 was 48,500 pounds, and it was hoped that this great expense might be lessened by such a change of operation. But the present Chief Engineer of the County Council, Mr. G. W. Humphreys, appears to question the true economy in doing this, although certain alterations in the plant are to be made.

The sewage enters the long settling tanks at Barking by large cast-iron gates set in the side. These gates are 6 ft. by 7 ft. 6 in. in size and are operated by hydraulic power. They are almost perfectly tight, although they have been in use twenty-five years without repair.

So, too, a somewhat elaborate rotary "grid" screen at the Crassness works has been in operation fifteen years and is still in good condition. These facts indicate care and good judgment in the original design and execution of the work.

While the river opposite the outlets did not appear foul, this was after a wet season. I was told that at times the oxygen content was very low, at one time not over 6 per cent, saturation, and the inference drawn was that further measures for protecting the Thames would be required before many years.

Before leaving London a visit was made to the new Chingford water storage reservoir near Enfield Locks, where the water is lifted by "Humphrey" gas pumps. The capacity of the station is 200 million Imperial gallons per day of 12 hours and the lift 31 ft. The pumps operate by the direct explosion of gas and air, admitted to a cylindrical receiver, on the surface of the water with which the receiver is previously filled. There are four such pumps at this station of a capacity of 28,000 Imperial gallons per minute and one of 14,000 Imperial gallons per minute capacity, housed in a building about 70 ft. by 140 ft. in size. A small producer plant is located adjacent, so that the entire installation is very compact, due largely to the fact that there are no boilers, no machinery and but few moving parts. The coal consumption is about one pound per horse power, and a 12-hour shift consists of a foreman and two men at the producer and an engineer and laborer at the pumps. The thermal efficiency of the pumps was said to be from 22 to 24 per cent.

*From The Polytechnic.

CALORIFIC VALUE OF EXPRESSING THE TRUE QUALITY OF GAS AND CONDITIONS GOVERNING ITS SUPPLY.*

The recent enactment, by the Public Service Commission of the State of Indiana, of rules regulating the quality and supply of illuminating gas, has prompted the preparation of a paper which will bring out some of the more important points and emphasize some of the conditions which have a direct influence on the manufacture of gas under a calorific standard. These conditions are particularly important at this time because the operation of some of your properties must necessarily be changed to conform with the prescribed standard, and in some plants will tend to increase the cost of manufacturing and supplying the gas.

In order to bring out some points relating to the most economic standard of gas quality, and to emphasize their influence on conditions in Indiana, it may be well to give a short historical summary of the development of the gas industry, with special reference to the changes in the quality of the gas supplied.

When gas was first produced by the destructive distillation of coal the crudeness of the apparatus, and inefficiency of the lighting appliances, resulted in a costly illuminant of poor quality. However, there was no complaint that the flames did not give sufficient illumination, as everybody was surprised that the so-called "inflammable air" gave any light whatever. As the commercial possibilities of the process were recognized, gas lighting became generally adopted throughout Europe and this country. In America, all of the large eastern cities adopted gas lighting in the first 40 years of the 19th century, and the incorporation of a company in Indianapolis (1852) marks the introduction of gas in Indiana.

The great growth of the gas industry, and experience and experimentation of those engaged in it, resulted in improvements in apparatus, in operating practice, in methods of distribution and utilization, which resulted in an improvement in the quality of the gas, with a coincident reduction of its cost to the consumer. Much experimental work was done, with the object of improving the types of installations, and to enable them to use the various grades of gas coals discovered. Every effort was made to better operating efficiencies, in order to reduce the cost and the selling price, and increase the business. These experiments and improvements, covering a long period of time, were based on the actual operation of many properties. While experimenting it was still necessary to supply gas at all times, and no doubt the quality was variable and frequently below normal. Had stringent restricting regulations been enforced during this time, based upon the normal or best quality of gas then made, many of these improvements and economies would undoubtedly have been retarded, if not altogether pre-

vented. Their absence stimulated operators to adopt every improvement, and to make every effort to better the efficiencies of their installations. It permitted old installations to be scrapped and improved systems to be erected in their place.

The most important improvement in gas manufacture to make its appearance in the 19th century was the carbureted water gas process, introduced in Phoenixville, Pa., about 1873. With the commercial adaptation of this process, the manufacture and distribution of gas for illuminating purposes received a new impetus. The principle had been known for some time, and the discovery of petroleum in large quantities, with a decrease in the price of its products, made available an agent to give luminosity to the non-luminous water gas. It was through the development of the patent of Prof. T. S. C. Lowe that this system of gas manufacture was placed on a commercial basis. The advantages of the carbureted water gas process over the older coal gas process were: Low cost of apparatus and operation, flexibility of operation, freedom from by-products (they were often difficult to dispose of), with the possibility of making a gas of any desired illuminating value within reasonable limits, and higher than that of coal gas. The supply of cheap oil brought the cost of carbureted water gas down to a figure that resulted in a wide-spread introduction of this process, both in towns already supplied with coal gas plants and in others previously considered too small to maintain a gas works, and the system made enormous strides during the 80's and 90's.

Previous to 1880 gas was practically used solely for illumination with open flame burners, and its quality was properly measured in terms of candle power. The ease of enrichment inspired operators to supply a water gas of high illuminating value, in order to better compete with coal gas installations, and to make gas lighting more attractive, hence a stronger competitor of electric lighting, then making its appearance. Not until after 1890 was much gas used for purposes other than illumination in flat flames, but about that time the perfecting of gas stoves, gas water heaters, and gas industrial appliances, caused the quantity of gas sold for cooking, heating and industrial work to increase so rapidly that it soon exceeded that sold for illuminating. In the field of illumination the invention and perfection of the incandescent mantle burner furnished a lighting medium, which, to a large extent, replaced the open flame, and this burner, giving from 4 to 8 times as much light per cubic foot as the open flame, is not dependent for its efficiencies upon the illuminating value of the gas.

As the value of gas for heating purposes was recognized, the bunsen or atmospheric burner became more generally used, being necessary where the flame comes in contact with, or impinges upon, a cooling surface. In its use it became apparent that a gas of high illuminating value did not give as satisfactory service as one of lower candle power, and that when hydrocarbon

*Abstract of paper prepared by Mr. J. B. Klumpp, Secretary Public Relations Committee, American Gas Institute, for the March, 1914, meeting of Indiana Gas Association.

vapors are present to a considerable extent, the difficulty of maintaining a perfect bunsen flame is increased. Unless the burner was exceedingly well designed, and provided for an ample supply of air, the combustion was incomplete, as with Welsbach burners when high candle power gas is used and any variation in quality or pressure occurs. In order to correct this trouble the candle power of the gas supplied was reduced. The high illuminating values were imparted to the gas by a percentage of hydrocarbons in excess of that which could be most efficiently used in Welsbach burners and other gas consuming appliances. With the realization that high candle power gas was not giving best service, and, with the consequent reduction in illuminating value which took place, a coincident reduction in calorific value was made.

About this time gas engineers began to appreciate that the illuminating value of gas no longer represented its true value to the consumer, but that its calorific (or heating) value did. Accordingly arguments were presented to regulatory bodies advocating that the standard of quality of gas be expressed in terms of its heating value, and several municipal bodies did establish such standards. Later, when state public utility commissions were established, their representatives confirmed the arguments presented by gas engineers.

The adoption of the calorific standard, as a regulatory order governing the quality of the gas, has been a very wise move, since this property of the gas represents its true value to the greatest percentage of its consumption. At the present time all gas, except the very small percentage used in the open flame burner, is used as a heating agent, and its direct value is expressed in terms of its total heating value, in British thermal units per cubic foot.

Gas calorimetry has been thoroughly investigated by a committee of the American Gas Institute, and by the National Bureau of Standards, and it has been proved that with calorimeters of approved type operated according to directions, the results obtained will be correct within 1 or 2 per cent; while readings of illuminating value may vary by as much as 50 per cent, depending upon the type of burner used, variations in the value of the standard, and the personal equation.

In changing from the candle power standard to the heating value standard now required, many operators are curious to know what relation exists between illuminating value obtained in the luminous flame burner, and heating value, and what calorific value corresponds to the candle power formerly supplied. Messrs. Dunbar and Davis have treated this subject in their able paper read before this Association in 1911, and proved that there is no definite relation between heating value and candle power, which has been corroborated by many recent experiments. However, for gases made by the same systems, those gases having the highest illuminating value have the highest calor-

ific value. The relation of these properties depends upon the constituents of the gas. For instance, if the illuminating value is produced entirely by the addition of such a low hydrocarbon as marsh gas (CH_4), we expect a heating value of 200 to 250 B. T. U. for each candle; whereas if the illuminating value is obtained through the medium of ethylene, we may expect a heating value of about 25 B. T. U. for one candle. If we increase the illuminating value by means of benzol we will find an increase of from 6 to 8 heat units per candle power added. Candle power, here, means flat-flame candle power. These figures of enrichment are approximate, however, and are affected to a considerable extent by the remaining constituents of the gas. For instance, an additional 1 per cent of carbonic acid (CO_2) will reduce the illuminating value of the gas by about 5 per cent, and the heating value by but 1 per cent.

The first State Utility Commission to specify a calorific value standard to the exclusion of the illuminating value, was that of Wisconsin, in 1908. At that time an investigation disclosed that the gas distributed in the state averaged over 600 B. T. U. per cubic foot, and, in order not to appreciably change the quality, the requirements were set at 600. At the present time the Wisconsin requirements are preventing the introduction of the more modern coal gas processes, through distributing unenriched, by-product, coke oven gas, and operating economies that would eventually be reflected in a reduction of price to the consumer. Several other states have followed Wisconsin's lead in adopting the heating value standard, and some have even adopted the same value. I believe, if these authorities had investigated the subject more fully, they would have appreciated that this standard restricted, to a considerable extent, the selection of gas generating systems, and of manufacturing materials. The Public Service Commission, Second New York District, realizing the importance of this, decided that an investigation of the prevailing conditions in that state would be a step towards the determining of the best standard of gas quality, and, therefore, solicited the co-operation of the engineers and operators of the state. The results of their 3 years' investigation have been published within the last year, and may be summed up in the following paragraph from the report:

"Taking all these conflicting factors into consideration, it is the judgment of the Committee that a total heat value, not exceeding 570 B. T. U., monthly average measured at the point where the gas leaves the manufacturing plant, corrected to a temperature of 60° F., and to a pressure of 30 inches of mercury, as measured by the rules of the Committee accompanying this report, is the standard which will best serve the interest of the people of New York State."

A perusal of this report will be of assistance in appreciating some of these facts, as a number of tests are given which show that unenriched coal gas, on

the modern settings, cannot at all times be made of a heating value as high as demanded in Indiana.

Because the standard adopted in Indiana is that of Wisconsin and some other states, it was thought advisable to point out that a standard suitable to one locality is not necessarily suitable for another. The conditions controlling the methods of production and supply of gas may be very different from those existing in another state, and many of these conditions are not apparent to the layman, and sometimes not to the operators, until a thorough investigation of local conditions is made.

The factors which determine the method of manufacture to be used are numerous. First, the quality of gas required by the state or municipal regulations must be considered, as these often limit the systems that may be employed; second, the availability of supply of manufacturing materials and their cost; third, the opportunity for disposal of the by-products; fourth, the investment necessary. In addition local operating conditions may influence the operator in selecting the process of manufacture, such as load factor, labor, conditions, etc.

Of these, all, except the state and municipal regulations, depend upon economic conditions. It is evident, therefore, that the regulatory bodies should so shape their orders that the manufacturer may be able to select those methods of manufacture which will enable him to make and deliver a serviceable gas at the lowest possible cost to himself, and, therefore, to the consumer. Any order that restricts the manufacturer prevents the highest economies being obtained.

We have spoken of the advantages and economics from the introduction of the carbureted water gas process, but within recent years conditions have changed very materially. During the past 10 years the demand for oil has increased enormously, with a steady increase in price, until the cost of carbureted water gas has, in many instances, increased to such an extent that, even considering the other advantages, it cannot compete with coal gas. While new fields are being discovered, the demand is increasing at a rate that will greatly restrict the use of oil for gas purposes. Within a few years all the navies of the world will adopt oil burning vessels, and a method by which the heavy fractions of petroleum may be broken down into the gasolines, etc., may be discovered at any time. These factors, and the increased demand for heavy oils for processes that can pay prices prohibitive to the gas industry, tend to hasten the time when most of the gas manufactured will be coal gas.

In supplying coal gas, the location with reference to the supply of coal, and the availability of a market for by-products, are probably the two most important factors affecting the quality of the product, and the cost of manufacture. High freight rates, on the higher grades of gas coals, will compel the use of poorer and more convenient low grades, resulting in gas of a lower quality. Where there is no profitable market

for coke, for instance in the anthracite coal region, the manufacture of coal gas is necessarily prohibited. It is the demand for coke that makes a coal gas or coke oven plant a success.

The more modern methods of coal gas manufacture, such as the vertical, inclined and through-horizontal retorts, include designs for the economical recovery for all of the by-products, and have overcome most of the objectionable features that were apparent in the earlier processes. The handling of the coal and coke is now by some form of belt or bucket conveyor, thereby reducing the manual labor to a minimum; charging or discharging retorts is either by gravity or some mechanically operated device; the size of the carbonizing chambers has thereby been greatly increased, and the cost of operation lessened. The result is that the operating cost of the modern installation is materially less than that of the older processes, but this saving is partially offset by interest and depreciation charges on the greater investment.

With improved apparatus the yield of gas per ton of coal has been increased, and the heating value per cubic foot of gas slightly reduced. Experiments by Mr. Thomas Goulden, President, the East Counties' Gas Managers' Association, presented in his presidential address, prove that, by increasing the yield of gas per pound of coal, a much greater total quantity of heat could be obtained in the gas. By reducing the heating value from 608 B. T. U. to 530 (a decrease of 12.8 per cent), he was able to obtain 32 per cent more gas, increasing the total heat delivered in the gas by 15 per cent. When it is considered that heat in gas is much more valuable than heat in coke, the economy of such operation is apparent. Besides lowering operating costs, by reason of extracting more heat per pound of coal, large yields reduce the total quantity of coke and other by-products and enable the operators to obtain a better price for them. All this shows that modern coal gas processes are economical, and their introduction should be encouraged by adopting a standard of heating value liberal enough to enable the gas produced to be distributed at all times without enrichment.

Another point to be considered in setting the standard is that, with the installation of large numbers of coal gas plants, the demand for gas coals will be greatly increased. The supply of high grade gas coal is limited, and any extraordinary demand will cause a rise in price. The United States Bureau of Mines, appreciating that the supply of such coals must soon become depleted, has conducted an investigation and showed that there are many coals somewhat lower in volatile combustible, which produce a satisfactory and serviceable gas, but a gas lower in heating value than that from the so-called "high grade gas coals." The reduction in cost possible by the use of these coals will often result in economies to the consumer in spite of a lower heating value. In order to enable operators to use such grades of coal, under the most economic

conditions, the calorific regulations should be set lower than 600 B. T. U.

Another economical process which gas companies should be permitted to take advantage of is the by-product coke oven plant. Any locality which offers a large market for coke is suitable for such a plant, and if the present rate of increase is maintained the surplus by-product gas available for urban distribution will soon amount to a large percentage of all manufactured gas. In coke oven operation the kind of coke required determines to a large extent the quality of coal that may be used, and practically confines it to grades that produce coke suitable for furnace uses. Such a coal is not what we term a "high grade gas coal," having only 22 to 28 per cent volatile combustible. The gas produced is not over 550 B. T. U., and under your present regulations could not be utilized.

In a number of places in this country coke oven gas is being supplied that has a high heating value, while in other cases the gas is much poorer. This difference is due to the type of ovens, the method of operation, and the treatment of the gas. When ovens were first installed in this country they all had a duplicate hydraulic main, by means of which the richer gases, or the first one-third driven off, were separated from the poorer or tail gases and for delivery to the gas company. This first fraction is high in heavy hydrocarbons or illuminants, has a high heating value, and its quality is easily controlled by varying the percentage of the gas selected for distribution, the remaining poorer gases being used for heating the ovens. In recent years many coke ovens installed do not thus separate the gases generated, the surplus gas sold for city supply being the run-of-oven, or a mixture of the poor and rich gases. Where ovens are so constructed the cost of the changes necessary for separation of the gases is prohibitive. If good grades of coals are used in such installations, the run-of-oven gas may be from 525 to 550 B. T. U., but under requirements 600 B. T. U., the use and sale of such gas are prohibited, unless some method of enrichment is adopted.

Whether, in new plants, the installation of a double hydraulic main and double systems for recovering by-products, will be profitable, depends upon the size of the plant and upon the percentage of surplus gas that can be sold.

Gas is the only by-product in coke manufacture that must be sold locally, and as fast as produced, and unless local gas requirements are large, the operators cannot afford to make any investment or change in operating methods to improve its quality. Not that the gas is not satisfactory for all domestic purposes; it is, and the supplying companies should be allowed to take it and distribute it without enrichment.

Coke oven gas and coal gas are often enriched with benzol to increase illuminating value, but while its use for candle power enrichment is satisfactory, the amount of heat obtained per candle of enrichment (6 to 8 B. T. U.) is so low that to raise the heating value

any considerable amount gives a gas too high in heavy hydrocarbon vapors, unstable in quality, unsatisfactory for general use, and, furthermore, very costly.

A description of the present conditions in Europe may be of interest, inasmuch as their present conditions are indicative of what may be expected in this country. In England about 90 per cent of the gas sold is coal gas, carbureted water gas, as a rule, being used only as a stand by. For some years the illuminating value requirements have been gradually reduced by governing authorities, until coal gas averages not more than 10 candles, flat flame, with a heating value of from 525 to 550 B. T. U.; and this is gas made from coals that are as good as the best gas coals in the United States. This low standard has been adopted after a scientific study of the subject, and upon determining that obtaining the greatest possible amount of heating the gas from a pound of coal is the most economical method of producing gas. Similar investigations, by German and other Continental authorities, have led them to adopt heating value standards low enough to allow the manufacturer to try various systems for coal gas carbonization, and have resulted in the development of a process of carbonization in bulk, which has made such strides that gas in these countries is being used for many purposes not possible in America.

These are the calorific standards of some foreign cities:

City	B. T. U. Average.
London	500
"	450
Tottenham	500
"	450
Berlin	543
"	522
Paris	550
Nancy	539
Rennes	570
Chatres	506
Valence	506
Marseilles	551
Milan	573
Buenos Aires	570
Colombo, Ceylon	400

One important point, frequently not considered when drawing up regulations, is that the requirement for testing gas at any place other than the manufacturing plant is unnecessary, and involves a duplication of work. When candle power standards were common, it was necessary to test the gas some distance from the plant, in order to insure the delivery of a uniform product to the consumer. With gas under a calorific standard, however, the loss of heating power in the distribution system is nearly constant for all seasons of the year, and if a uniform quality of gas is sent out from the plant, the consumer may be sure of gas of a uniform quality. Regular tests of the gas quality must be made at the plant to operate efficiently, and tests required at an outside point only mean that this work must be duplicated, entailing additional expense without benefit to consumer.

Whatever differences of opinion may exist in re-

gard to the best method, the common aim of state commissions and gas companies is the supply of serviceable gas to the consumer at the lowest cost. It is the opinion of the writer that a standard lower than 600 B. T. U. will most economically serve the interests of the people of this and all the other states.

SOME INTERESTING TESTS OF FILTERED OIL.*

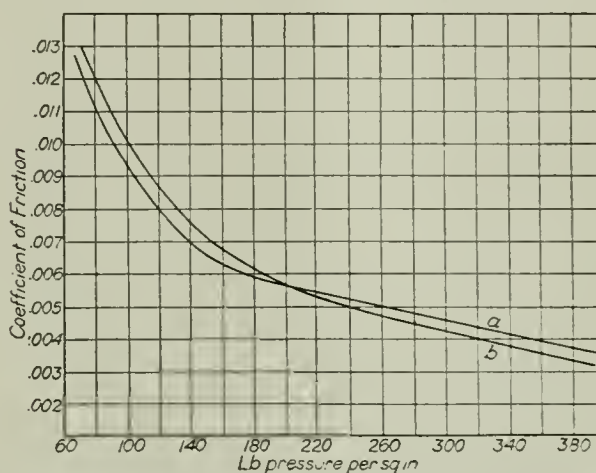
To determine exactly what deterioration lubricating oil suffers when in constant use, the Richardson-Phoenix Company, Milwaukee, Wis., recently had a rather elaborate series of tests made on different samples of oil at the laboratories of Cornell University. It was proved by these tests that if oil is properly filtered it can be used over and over again indefinitely without losing any of its lubricating qualities. The samples were selected from a number of plants, and the data secured from the test of the oil used at the Hotel McAlpin, New York City, has been selected as representing the most severe operating conditions.

The power plant of this hotel is equipped with a Richardson central oiling and filtering system, supplying lubrication to four engines, four air compressors and a crank and flywheel pump with a grand total of 134 points of lubrication. The plant operates continuously, and the average temperature of the engine room is 100° F. On account of the great variety of machines lubricated, the high load factor and the exceptional temperature conditions, the work imposed on this lubricating system is probably as severe as can be found in any power plant. The average amount of oil handled by the lubricating system was 150 gallons per hour, or about 1,800 bbls. per month. Although this large amount of oil is supplied continuously to the bearings, it is stated that it is only necessary, in this plant, to add about 3 bbls. of oil per month, and even this quantity cannot be charged to natural shrinkage in the system, as large quantities of oil are drawn off from the filters and used in cans for the hand oiling of small pumps, valve gears and other bearings not connected with the oiling system.

To determine the changes undergone by the oil, a sample of new oil, as received in barrels from the manufacturers, was secured, and a sample of oil was also drawn off from the clean oil compartment of the filter. These were sealed in the engine room and shipped to the testing department of the university, where a series of tests were made without any further purification or filtration. A number of friction tests were made on a railroad lubricant tester, having a hardened steel journal and bronze bearings with a total area of 20 sq. ins. In all the tests, the testing machine was run at a constant speed of approximately 360 r. p. m., and the load applied in increments of 75 lbs. per sq. in., until a total pressure of 1,500 lbs. was reached. The

test at each load was continued until the friction and temperature of the bearing was constant. The oil was fed upon the side of the bearing through a sight feed oiler, and the feed maintained as nearly constant as possible throughout the tests. The results of the tests for the coefficient of friction are presented in the accompanying diagram, the new oil being shown in the curve *a*, while the filtered oil is represented by the curve *b*.

Tests were also made to determine what physical changes, if any, had taken place in the oil, which had been used in the system for over 18 months. It was found that the oil had gained in specific gravity through constant use, which was to be expected, as the oil in passing through the bearings had had some of its more volatile constituents driven off. The tests for viscosity showed that the used oil had a higher value than the new, thus demonstrating that as the oil

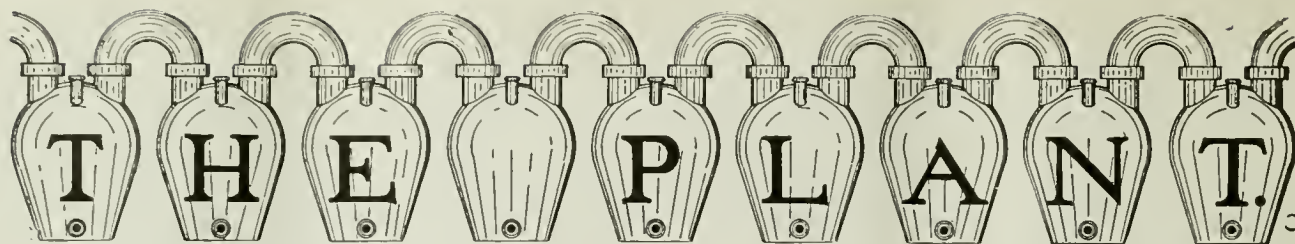


Results of Tests Made to Determine Coefficient of Friction of New Lubricating Oil and the Same Oil After It Had Been Used.

is used over and over again in the oiling system it actually gains in body, provided, of course, that the entrained water is entirely removed by the filter. It will be noticed that the new oil has a slightly lower coefficient of friction on low bearing pressures, while the purified oil shows a lower value on higher ones. This is due to the fact that the old oil has more body and is thus better able to maintain a lubricating film when subjected to higher pressures. The difference between the two curves, however, is so slight that for all practical purposes properly filtered oil is as good a lubricant as new. A set of curves to show the difference between the temperature of the bearing and the room were practically superimposed, and in no case was the variation more than a few degrees.

The United States is making increased purchases of vegetable ivory nuts for manufacture into buttons. Imports in the fiscal year 1908 totaled 14½ million pounds, in 1912, 23 million pounds, and in 1913, 20 million pounds. They are nearly all derived from Colombia and Ecuador, the latter country alone furnishing nearly 17 million pounds in 1913.

*From The Iron Age.



CASEIN IN PAPERMAKING.*

In the manufacture of coated papers a mineral pigment, either white or colored, is mixed with an adhesive and spread by special machines as uniformly as possible over the surface of a web of paper. The function of the adhesive is entirely that of binding the pigment to the paper, so that it will not be removed by the type or plates during the printing process. For this purpose casein is very largely used, having in fact almost entirely replaced glue, which for many years was used for this work, practically to the exclusion of all other materials. A description of the process of manufacturing and testing casein, with an account of its use in the coating of papers, is given by E. Sutermeister in the *Pulp and Paper Magazine*.

Casein is present in milk to the extent of about 3.0 per cent, and may be prepared from it either by the action of rennet or by means of acid. Since the rennet casein is difficultly soluble and is not used in the coating industry, it will not be considered here. Acid caseins may be prepared either by adding acid to the milk or by allowing it to sour naturally. The former method is largely employed in this country while in South America the latter method is the most general.

The procedure in making an acid casein may be briefly described as follows: The skimmed milk, from which the fat has been removed as completely as possible by centrifugal separators, is run into large, rectangular, wooden vats, and heated to about 120° F. by blowing in live steam. To this warm milk dilute acid is then added in amount sufficient to slightly more than precipitate all the casein; at this temperature the clots of casein adhere to one another so that the whey can be readily drawn off. Hot water is then added, the steam turned on and the curd washed by working it over with wooden rakes. When this wash water is drawn off the curd is found to have drawn together into a tough, doughlike mass, and this is taken out of the vat, cut up into large pieces and allowed to drain on slanting boards or racks. This drained curd is then run through a disintegrator, which shreds it quite fine, and the shredded material is spread on wire-covered racks and dried in a current of warm air. In making self-soured or natural-soured casein as it is sometimes called, the curdling is caused by the natural production of the lactic acid. When thoroughly curdled the whey

is removed by pressing in burlap bags and the pressed curd is then shredded and dried as usual.

The method employed and the care which is exercised throughout the operations are largely responsible for the grade of casein turned out. Muriatic acid gives quite a different product from sulphuric acid, and the self-soured is not exactly like either in its working properties. If the wet curd is not promptly dried it becomes mouldy and of inferior color and strength, and the same result is caused by too low a temperature in the drying galleries, which means that the curd must be left in them for an unusually long time under the best possible conditions for spoilage. On the other hand, if the drying temperature is too high, the casein turned out will contain a large proportion of red or orange-brown particles and its solubility is much impaired. Other conditions which tend to cause a low grade product are frequently present since it is often considered a by-product by the dairies or creameries producing it, and so gets attention only when the men can be spared. As it is necessarily produced in greatest quantity when the milk supply is greatest, and the dairy the busiest, it is often neglected. Then again, the drying plant is expensive, so that one central plant is made to handle the green curd from a number of surrounding dairies; and during transportation, especially in summer, this green curd has an excellent chance to deteriorate.

The caseins on the American market are received from France, Italy, Sweden, Russia, Denmark, and South America, as well as from numerous local sources. Since all sorts of processes are employed in these countries, and the care used is entirely problematic, it is evidently very desirable to have some method by which casein can be tested and its value determined. Although no entirely satisfactory tests, which can be applied by both the producer and the consumer, have as yet been advised, there are certain methods which are well worth considering.

In 1912 Hopfner and Burmeister published a number of analyses of technical caseins from which the following figures for moisture, fat, ash, and nitrogen have been taken:

	Maximum Percent	Minimum Percent	Average Percent
Moisture	10.50	7.27	9.23
Fat	2.06	0.23	0.85
Ash	4.95	3.53	4.07
Nitrogen in sample as received	13.55	12.52	12.99

For comparison with these are given the following

*From Paper.

results obtained by the writer on numerous shipments of goods received in the American markets:

	Maximum Percent	Minimum Percent	Average Percent
Moisture	12.3	5.4	9.64
Fat	9.9	trace	3.68
Ash	4.5	1.0	3.29
NaOH to make neutral to litmus.....	3.8	1.30	2.51

The wider variations in the American goods are probably due to the wider field from which they were drawn, as they are known to include a number of foreign caseins as well as a great many of domestic manufacture. The much higher percentage of fat may be due to actual difference in the caseins, but is more likely to be caused by the methods of analysis. Hopfner and Burmeister determined the fat by extraction with ether and petroleum ether which, in the hands of the writer, has been found to be very tedious and quite inaccurate, a portion of the fat always remaining with the casein. The results on American goods given above were obtained by a modification of the Babcock milk test, which was found to be more accurate and much more rapid.

In addition to these chemical tests, most of these shipments were carefully watched during use, and it was found impossible to trace any connection between the practical results and the analytical data. For this reason it was felt that small scale tests which would more nearly duplicate actual working conditions, would give more reliable information than could any chemical analysis, and the rest of this paper is devoted largely to a discussion of such tests.

Casein is a body of an essentially acid character, which is insoluble in the water; the addition of alkali, however, neutralizes the acid and forms a compound which may be considered as a caseinate of the base employed. The caseinates of ammonium, sodium, potassium and lithium are soluble, while those of the heavy metals are not, but since the latter do not come into consideration in the coating industry, and since, for reasons of expense, lithium and potassium are never employed, we are concerned almost entirely with solutions prepared with ammonia or some of the compounds of sodium. Of the latter the silicate, sulphite, phosphate, hydroxide, carbonate, borate, etc., have been proposed and used from time to time, but while the phosphate, carbonate, and borate are still very generally used the other three are not commonly employed. As a standard solvent for use in testing, we have then the choice of four alkalis, but because of the difficulty of handling ammonia and of keeping it at a definite strength it is practically debarred. Of the three sodium salts the carbonate has the disadvantage of causing much foam, which necessitates extra care in making the test, while the other two are easily obtained of good purity and are of about equal solvent power. There is really very little to choose between these two, but since borax has been for a good many years the alkali most used in solubility tests, there seems to be no good reason for changing now.

The specifications for solubility under which one of the largest concerns formerly purchased its casein were about as follows: One part of casein mixed with four parts of water and 15 per cent of borax (on the weights of the casein) when heated to 150° F. and stirred three minutes, should be completely dissolved when allowed to stand for half an hour. This test is thought to be too severe in several ways, and if it is strictly adhered to will cause the rejection of many caseins which will work perfectly in practice. The time of heating and stirring is not long enough, and the temperature may go much higher than 150° F. without bad effects, provided the heating is not very prolonged. There are also found occasional lots which will not dissolve with less than 18 per cent of borax, though with that amount the solution is perfectly satisfactory.

As a substitute for the foregoing specification, the following is suggested:

The sample of casein should be ground so that all of it will pass a 20-mesh screen, and after grinding the entire sample, should be thoroughly mixed. Of this ground casein 100 parts should be mixed with 400 parts of water and 15 parts of commercial borax and the mixture heated and stirred till solution has taken place. In making this test the following precautions should be observed:

At least 50 gm. of casein should be taken for each test; the heating must be by means of a steam or water bath, and blowing live steam directly into the mixture should not be practiced; the temperature at which the solution is made should not exceed 180° F., nor the time of stirring 10 minutes. A casein to fulfill this test must give such a complete solution that no undissolved particles are observed when the solution is stirred in a glass vessel or when a clean knife-blade is dipped to the very bottom of the solution and then withdrawn.

Nearly all of the high grade caseins of the present day will pass this test, though, as noted, there is an occasional lot which requires slightly more alkali. There is also another class of caseins which, when tested in this way, show a little insoluble residue, generally in the form of white flakes, which may or may not dissolve on further heating, or the addition of a little more alkali. The acceptance or rejection of a casein of this class depends on the particular purpose for which it is to be used, and on the judgment and experience of the one in charge of the tests, and it is not possible to lay down a general rule which may be followed in all cases.

The next quality to be considered in judging a casein is its strength.

As already stated, the purpose of the casein is simply to make the clay, or other mineral matter, adhere to the paper, so that its strength may be stated as the amount of casein required to make a given amount of clay adhere so firmly to the paper that it would not be removed by ordinary printing processes. By many, the strength of a casein has been considered to be pro-

portional to the thickness of its solution or to the firmness of the so called jelly formed when the solution is cold. Still, others judge by the length of threads formed when the solution is pressed between the thumb and finger and then pulled apart, that which gives the longest threads being considered the strongest. Many careful comparisons have failed to establish any definite relationship between such tests and the actual amount of casein used in practice, so that a more rational method was desired. The details of such a test, which has been used by the writer for many years with excellent satisfaction, are briefly as follows:

One hundred grammes of clay, previously dried at 100° C., are weighed out into a thick-walled porcelain cup, 70 c.c. of water are added and the cup set aside to allow the water to saturate the clay. While this is taking place 50 gm. of casein are weighed into a tared beaker, 190 to 200 c.c. of water are added, and then the amount of alkali which has been found to give a complete solution is stirred in and the solution completed by heating on a steam bath. If 200 c.c. of water, or a little less, are used, the final solution will weigh a little less than 250 gm. and it should then be brought up to this weight by adding hot water, so that each gramme of casein is represented by 5 gm. of solution. The clay and water are next thoroughly worked up to a smooth paste by means of a copper rod which has been flattened into spatula form for a distance of about three inches, and which has had the flattened end turned over nearly at right angles to enable it to work out lumps which may settle on the bottom of the cup. The cup, clay and copper spatula are weighed and then enough of the casein solution (30 gm.) poured in to equal 6 gm. dry casein. This is then thoroughly mixed with the clay, and a thin coating applied to a small sheet of paper which is then marked "6" and put aside to dry. The cup and its contents are once more balanced up and 5 gm. more solution added and mixed in; the sheet spread with this is marked "7." This process is repeated till the amount of casein reaches 11 parts for the original 100 parts of clay, and unless the casein shows unmistakable signs of poor manufacture or subsequent deterioration it is seldom necessary to carry it further.

In spreading the sheets for this test a brush may be used, but it has been found more convenient to apply the coating by means of a thin steel scraper, which is made from an old saw and bent into an arc, so that it may be held in the hand and drawn across the paper with its surface nearly parallel to the latter. The edge of this scraper must be ground perfectly true and smoothly polished so that it may not leave scratches; it should also be as light as possible, otherwise it will be difficult to regulate the amount of coating applied. When using this scraper the paper should be supported by a perfectly flat surface, such as a machined brass plate, so that the coating may be applied uniformly.

When the individual test sheets are thoroughly dried they are inspected and two positions selected on each

in which the coating appears of a uniform thickness on looking through it at a strong light. After marking these positions, a short stick of sealing-wax is melted on one end, applied to the paper with a moderately firm pressure and allowed to stay till fully cold. The melting of the wax may be done by means of a gas flame if care is used to see that it does not burn, but a better way is to make a copper box with a flat top, which can be heated by blowing steam into it, and to stand the pieces of wax on end on this box till they are sufficiently melted to adhere to the paper. When the wax is cold the paper is held down firmly by a finger on either side of the wax and the latter is removed by a steady vertical pull. If insufficient casein has been used the surface of the wax will be covered with a thin film of clay, but no fiber. When enough casein is present, the fibers of the paper will be found adhering to the wax to the very edge, while at the transition point between weak and strong, the wax will show fibers in the center, but an edge which is bare, except for clay. A characteristic record for a casein of good grade would be about as follows:

Six grammes per 100 of clay—clay but no fiber adheres to wax; too weak.

Seven grammes per 100 of clay—fiber in center, but clay only on edges; the transition point.

Eight grammes per 100 of clay—fibers adhere over full surface; strong enough.

This casein would be said to be strong enough with between 7 and 8 parts per 100 of clay.

In interpreting this test, it must be remembered that it does not mean that in practice 7 to 8 lb. of casein will hold 100 lb. of clay, and give a coating which will print without picking, for it is found that owing to the different conditions in coating paper on a large scale, a much larger amount will be required. It has, however, been repeatedly demonstrated that the strengths as shown in the laboratory tests are directly proportional to the amounts which it is found necessary to use in actual work, so that if one casein tests 8 parts and another 10 parts per 100 of clay in the laboratory, it is perfectly safe to say that the manufacturer of coated paper will have to use more of the latter than of the former to produce the same result. It is on this basis, as a strictly comparative test, that the method justifies itself.

In performing his strength test a number of precautions must be observed, since if they are not the value of the test, even in a comparative way, is very slight. It has been found that the quality and fineness of the clay used exerts a remarkable influence on the test, the finer clays requiring much more casein than those of coarser texture. This necessitates keeping a supply of clay on hand, and before this is gone selecting another sample by comparison with the first so that it may be certain the new gives the same test as the old. This is not always an easy task and it is sometimes necessary to make strength tests with the same casein on a half-

dozen different samples of clay before the proper supply can be secured. This same method of testing has to be applied to the paper used when the old supply runs out, only in this case both the casein and clay are the same, and the paper to which they are applied varies. The causes which make the papers differ in the amount of casein required to hold clay on their surfaces are not entirely known, but some of the contributory causes are variations in sizing, surface finish, and the beating of the fibers. Even with a knowledge of the way in which these factors influence the results it is not always possible to tell what a given sample of paper will do, so that the only satisfactory way is to make a practical trial. Another point to which attention must be paid is the thickness of the coating applied, as this has a considerable influence on the wax test. It is often found that the thicker portions of the coating will give a much lower strength than the thin parts on the same sheet, and this is the reason for the careful selection of points of uniform thickness when applying the wax. There are undoubtedly other factors which exert some influence over this test, but these three are the most important, and if the precautions noted above are carefully observed, the test will give concordant results.

It might be argued that a test which is so sensitive in several of its essential elements would be impossible of practical application, but it has been found that the same observer can readily duplicate his results and even that two different observers working in the same laboratory and with the same materials can obtain practical checks. It is, however, quite evident that unless standardized clay and paper are supplied from a central depot and personal instruction given in the method of making the test, the results of different workers will not be the same, though with a given series of caseins there should be a constant difference, *i. e.*, one series of tests should be consistently higher or lower than the other. Lack of consideration of these facts is likely to lead to confusion and differences of opinion, and the test is, on the whole, not one which can be generally applied by both manufacturer and user of casein or which could be included in specifications for quality. It is, however, of great value to the producer of coated paper, and can well be adopted by all who desire to keep their casein consumption at a minimum.

The question of the moisture in commercial caseins has been touched upon in the preceding portion of this paper where it was stated that goods in the American market contained on an average about 9.64 per cent, and that the maximum observed was 12.3 per cent. If much more than this is present the casein is very difficult to grind, as it appears more or less elastic and therefore resists crushing. This tends to set a practical limit to the amount of moisture which can be left on drying a casein, and intentional moistening as a means of increasing the weight is probably never practiced because of the danger of its spoiling subse-

quently. As it is, nevertheless, occasionally desirable to determine the moisture present, it is well to note the possible methods and conditions.

The most common procedure is to dry a sample at 100 to 105° C., and if this temperature is maintained for 2½ to 3 hours, the weights will be found to be practically constant. A long series of tests showed that different caseins do not behave in exactly the same way on drying, but in general, it may be said that sufficient decomposition of the casein to cause an appreciable error does not occur below 115 to 120° C., and that exposure to 105° C. for as long as 18 to 20 hours does not vitiate the results.

Another method which is capable of giving just as accurate results in a shorter time is that of distilling from a flask in which the casein is covered with water-saturated xylol or toluol. The distillate is collected in a graduated vessel, and the water which settles to the bottom may be read off directly in grammes.

It is fully realized that the methods of testing described in this paper do not, on the whole, assist materially in drawing up specifications for casein, but they are probably the best which have yet been proposed for use by the manufacturer of coated papers. Since, from the standpoint of both producer and consumer, it seems very desirable to have standard tests, by which it may be accurately graded, it is hoped that this discussion may encourage others to describe similar attempts to solve this problem.

RUBBER SHIPMENTS FROM AMAZON VALLEY.

The decline that marked the shipments of crude rubber from the Amazon Valley in the first half of the current crop year continued during January states exports declining during that month by 2,877,799 lbs. when contrasted with shipments in January, 1913, the loss in cargoes to Europe being particularly heavy, as the following table shows:

Exported via—	To United States. Pounds.	To Europe. Pounds.	Total exports. Pounds.
Para	2,264,586	1,694,594	3,959,180
Manaos	1,442,345	1,704,766	3,147,111
Itacoatiara		59,370	59,370
Total, January, 1914	3,706,931	3,458,730	7,165,661
Total January, 1913	4,633,208	5,410,252	10,043,460
Decrease	926,277	1,951,522	2,877,799

The feeling here is that the crop year which ends June 30, 1914, will show total shipments 10 to 30 per cent below those for the preceding season, these estimates being based on the decrease in supplies that have been sent up river. Prices still continue to rule low, but toward the end of January there was a more buoyant tone to the market and a general belief that prices would rule higher before March.

POWER ECONOMIES IN GAS PLANTS.*

ECONOMICAL STEAM PRODUCTION.

(A) *Fuels*.—Selection of the most economical fuel for a boiler plant is one of the most important questions for the operating engineer, and is often decided for him by location.

Boiler fuels may be divided into three general classes:

Solid: Natural.—Coal, wood and peat.
Prepared.—Charcoal, briquettes and coke.
Liquid.—Oils and tars.
Gaseous.—Natural gas, producer gas, oil gas and commercial gas.

We are most interested in solid fuels, as oils and tars are generally too valuable for use under boilers, and gaseous fuels are little used, as they can be employed with greater efficiency in internal combustion engines.

Coal is the fuel most used for steam production, and exists in various forms from a comparatively recent cellulose growth, such as lignite, to that of anthracite coal, which is nearly pure carbon. They are usually classified according to the proportion of volatile matter as follows:

Anthracite	Vol. Matter	3 to 7 per cent.
Semi-anthracite	"	7 to 13 per cent.
Semi-bituminous	"	13 to 25 " "
Bituminous	"	25 to 50 " "
Lignite	"	50 per cent. and over.

Anthracite is almost entirely carbon, is slow burning, gives practically no smoke and contains very little ash or inorganic matter. Semi-anthracite burns more freely than anthracite, does not cake or clinker to any extent, but requires considerable draught to properly burn it, and is expensive and difficult to obtain.

Semi-bituminous is probably the best steam coal. It is fairly free burning, requires only a moderate draught, is generally low in ash and, although a coking coal, does not clinker badly, but gives some trouble from smoke unless burned in properly designed furnaces.

Bituminous coals are also used to a great extent. They vary greatly in composition and to be satisfactory must be burned in correctly designed furnaces.

Lignite is seldom used as a boiler fuel, as it is too high in volatile matter and moisture, except where the price of other coals is prohibitive.

Coke, except in the form of dust or breeze, is too valuable for use under boilers, as are also manufactured fuel briquettes.

Choice of Fuels.—Generally the fuel that will give the greatest value in B. T. U.'s per dollar will prove to be the most economical. Where several fuels have a nearly equal B. T. U. value per dollar, it may be well to consider other things. Some plants have a choice of small sizes of anthracite, semi-bituminous and bituminous coal, and of many grades of each. First settle the kind of coal, and then the particular grade which will give the greatest efficiency.

In considering the first question, the equipment of the boiler plant must first be considered. Furnaces designed for anthracite coal are seldom efficient for semi-bituminous or high volatile coal. Grates designed for one kind of coal are seldom satisfactory for another, and the available draught must be considered as affecting economy and capacity. The relative cost of handling to the boiler room, fire room, labor, and ash handling must be considered, as a cheaper fuel high in ash may require as much as 50 per cent more labor in handling.

The question of smoke nuisance is important in many cases, and becoming more so each year. Bituminous coals cannot be burned without smoke except in specially designed furnaces or by good mechanical stokers.

The most satisfactory method of determining the relative efficiency of coals that appear to be equal in B. T. U. per dollar, is by carefully conducted comparative tests on individual boilers, or preferably on the entire plant, using each grade of fuel for several weeks.

After the kind of coal has been selected there usually is a choice between different mining regions or different mines. The usual practice is to buy on a B. T. U. basis, determined by calorimeter test on average samples. This method is not entirely satisfactory, as samples are usually better than the general run. In addition to their B. T. U. values, the proximate analyses of samples should be considered, especially moisture, volatile combustible and ash content, and fusing point of the ash.

(B) *Feed Water*.—The function of a steam boiler being the evaporation of water into steam by transfer to the water of the heat units in the coal burned, it is desirable to understand the peculiar properties of waters and the effect of the contained foreign matters upon the boiler itself, and on its efficiency as a steam generator; and also the methods used to rid boiler feed waters of such objectionable matter.

All natural waters contain some foreign matter in suspension or in solution, but there is great difference in quantity and in their chemical action at high temperatures.

Impurities in boiler feed water cause three kinds of trouble:

1. Incrustation, or the formation of scale on the water side of the heating surfaces. This is caused by:
 - (a) Mud or other suspended matter.
 - (b) Soluble salts.
 - (c) Bicarbonate of lime or magnesia.
 - (d) Sulphate of lime.
2. Corrosion of the metal in the boilers can be caused by:
 - (a) Acids.
 - (b) Chloride or sulphate or magnesium.
 - (c) Grease or oil.
 - (d) Organic matter.

*Abstract of report of committee presented at the 8th Annual Meeting of the American Gas Institute.

- (e) Dissolved carbonic acid and free oxygen.
- (f) Electrolytic action.
- 3. Priming or foaming in the boiler may be due to:
 - (a) Oil.
 - (b) Scum on the surface of the water formed by sewage or other light suspended matter.
 - (c) A large excess of carbonate of soda or other alkali.

Scale forming is a source of danger if allowed to continue until it interferes with transmission of heat to the water. Scale may cause bagging of the shell plates, above the furnace, and serious accidents. In water tube boilers it may cause blistered tubes, involving replacements and serious accidents. It is unusual to find boilers in operation having dangerously heavy scale, but even thin scale may prove a source of loss and danger, especially in water tube boilers, operating at high ratings, as loose pieces of scale may pile up, preventing water from coming in contact with the tube. This is a common cause of blistered tubes, and they usually show a pile of loose scale at the point where the blister formed.

Scale also causes loss of economy but it is difficult to obtain reliable data on the effect of different densities and thickness. Manufacturers of boiler compounds and feed water purifiers would have us believe that even a very thin scale causes considerable loss, and while this may be true, the loss is not as great as often stated, for most forms of boiler scale are fairly good conductors of heat, and it is doubtful if scale under 1/16 inch in thickness will cause much loss in efficiency. As a rule a soft, porous scale causes greater loss than one hard and dense.

The following from tests made at the University of Illinois, give an idea of the effect of scale on economy, but there is so much difference of opinion on this subject that the figures should be used with caution:

Thickness of Scale In.	Character of Scale.	Per Cent Decrease in Conductivity Due to Scale.
0.033	Soft	4.3
0.033	Very hard.	3.5
0.04	Soft, porous.	6.82
0.04	Hard, dense.	3.07
0.07	Soft.	2.38
0.07	Hard.	4.43
0.085	Soft, porous.	19.0
0.089	Very soft.	4.95
0.11	Hard, porous.	16.73
0.13	Hard, dense.	6.75

The important facts to be remembered are that the scale in boilers is not only expensive in repairs and dangerous, but does cause loss of efficiency which may amount to 20 per cent.

Corrosion in steam boilers is a source of danger and loss.

Priming is more dangerous to the machinery using the steam, than to the boilers themselves, but it may also cause loss of economy. If engines have efficient steam separators and the steam lines are well drained, the boilers may prime badly without danger to the plant, but the heat loss from water which has been raised to the temperature of steam and is removed

from separators and pipe lines, may be considerable. The cause of priming can usually be detected and removed, and a good boiler, even when operating at high overload, should deliver steam with not more than 1½ per cent of moisture.

Blowing Down.—In the generation of steam, pure water only is removed from the boiler as steam, and most of the impurities remain. As the process advances, new water containing impurities continually enters the boiler, and they remain when the water is evaporated into steam. Some of the concentrated impurities are deposited as scale and some remain in solution or as suspended matter. Blowing down a boiler will reduce the concentration, by removing water containing an excessive amount of impurities and allowing fresh water to take its place, but the quantity blown out at any one time is only a small percentage of the total water in the boiler. Some soft sludge and scale also are removed by blowing down, but not enough to prevent scale formation. Considerable heat is lost when water at the temperature of steam is blown out, and if a boiler were blown frequently enough to lessen concentration, the loss would be great. It is advisable to blow down at regular intervals to remove sludge from around the blow off, but it has little effect on scale formation, corrosion or priming.

Mechanical Cleaning.—Scale can be removed from boilers by mechanical cleaners or scrapers, and this is the most economical method, where good water is used and only light scale formed. In plants using bad feed water this method is expensive and unsatisfactory, as these cleaners are expensive to keep in condition, dangerous to the tubes if not properly handled, and usually leave a light coating on the iron. Scale removal mechanically means idle boilers during cleaning, extra labor dismantling boilers and cleaning, injury to fire brick arches, and power to operate cleaners.

Heating Feed Water.—There is unquestioned economy in heating feed water with exhaust steam, but without chemical treatment it has little effect on scale formation. Some of the carbonates are precipitated in water heaters, if heated above 200° F., but it is likely to be gradual and take place not only in the heater but in the feed lines. If the water is treated with the proper chemicals and a settling tank used to allow time for the chemical reactions, and an efficient filter to remove the suspended matter, the system will be fairly reliable purifier for some waters.

Boiler compounds are usually composed of lime and soda ash, with other substances which may or may not add to their value. Compounds may be either introduced into the heater, in which case they are likely to be inefficient unless a proper settling chamber gives them time for reaction, or direct into the boiler, where they cause increased precipitation and formation of soft sludge which may be more injurious than hard scale, though easier to remove. They are often a help in maintaining plant capacity and in reducing cost of boiler cleaning as they help prevent hard scale, but it

is doubtful if they increase operating efficiency.

The proper method of purification of feed water is by the chemical treatment before it enters the boiler.

There are several purification systems on the market that are efficient, if properly operated. The question for each case, is, can a great enough increase in economy be obtained to cover interest, depreciation and maintain charges on a purification system.

A purification plant can be installed for from \$1.50 to \$3.50 per horse power and the cost of chemicals for purification ranges from 1 cent to 4 cents per 1,000 gallons. Most systems require little attention and no additional operating labor charges, and their depreciation and maintenance charges should not exceed 8 per cent.

The saving by the use of purified water depends largely on local conditions, but in most cases the following can be effected:

(a) Increased life of boilers. Corrosion is reduced and wear on tubes and shells, due to frequent cleanings.

(b) Increase in time of operation of boilers in a given period. Less time out of service for cleaning and repairs, and fewer reserve boilers required.

(c) Saving a maintenance of settings and other brickwork, injured during cleaning, and by frequent cooling and reheating.

(d) Saving in pipe and fitting replacements, necessary when scale forms in them.

(e) Saving in valves and fittings throughout the plant. Steam always carries some entrained moisture, and this contains concentrated impurities.

(f) Saving cost of compounds, if previously used.

(g) Saving in labor for opening up and closing boilers, and for cleaning.

(h) Saving of repairs to mechanical cleaners.

(i) Saving power used for operation of cleaners.

(j) Saving in fuel due to clean heating surfaces.

Heating Feed Water.—At usual steam pressures and heater inlet temperatures there is an increase in economy of 1 per cent for every 12° rise in temperature of the water in the heater.

Closed heaters are usually located on the discharge side of the feed pump. Open heaters are placed on the suction side of the pump, and high enough to give sufficient suction head to prevent vapor forming in the suction pipe or water end of the pump.

Open heaters have back pressure valves, and may be injured if these valves fail to open. Closed heaters are designed for pressures far in excess of the working pressure, and do not rely on valves to protect them.

In open heaters water can be heated to the temperature of the exhaust steam. In closed heaters the temperature of the water never quite equals that of the steam. Oil and scale soon coat its tubes and reduce the efficiency of the heater.

Open heaters are easy to clean and most types of closed heaters difficult.

Oil in the steam mixes with the water in open heat-

ers and cannot be entirely removed, while in closed heaters no oil enters the feed water.

(f) With open heaters the water must be pumped into the heater, and then from the heater to the boilers, which is uneconomical, especially as hot water has to be pumped.

In spite of the disadvantages of the open heater given, it is usually preferred on account of its greater maintained efficiency.

(C) *Boilers.*—Boilers are divided into two general classes—fire tube, in which the gases of combustion pass through the tubes, and water tube, in which the water circulates through the tubes and the gases pass around the outside of the tubes.

In considering power economies it will be assumed that boilers are properly designed for efficient steam generation, and only those features liable to changes during operation, and which prevent the boiler from absorbing a maximum quantity of heat from the fuel burned, will be considered.

Causes of Inefficiency of Boilers.—(a) Scale or sludge deposit on the water side of the heating surfaces, which decreases the heat absorptive efficiency.

(b) Deposit of soot, dust or carbon cake on fire side of heating surfaces which decreases the rate of heat absorption.

(c) Inefficient baffling, which allows the furnace gases to pass out at high temperatures.

Losses Due to Foul Heating Surfaces.—It has been shown that scale formation will adversely affect boiler economy. But though some forms of boiler scale are poor conductors of heat, carbon in the form of cake or loose dust is a worse conductor. It is generally understood that scale is dangerous, and care is usually taken to prevent its becoming so heavy that the boilers might be injured. But soot and carbon deposit can be allowed to accumulate until the gas passages or tubes are so choked that the draught is almost shut off, and heating surfaces so foul that the preventable loss of sensible heat in the escaping stack gases is greatly increased.

It has been found that the loss due to a carbon deposit, 1/16 inch thick, may amount to as much as 20 per cent. Steam jets will remove loose dust and soot from a boiler and will reduce the rapidity of carbon cake formation, but they will not altogether prevent it.

Mechanical Cleaning of Heating Surfaces.—If boilers are to be kept in the best condition this carbon deposit must be removed at regular intervals, and should have the dust and loose soot removed by frequent blowing with steam jets while in operation. Mechanical cleaning may be accomplished by the following methods:

(a) By brushing off surfaces with wire broom.

(b) By specially designed scrapers.

(c) By knocking or hammering with a rod or pipe.

(d) By filling the boiler with cold water and pass-

ing steam over the fireside of the surfaces, causing the carbon deposit to crack and drop off.

(c) By the use of a mechanical cleaner, which causes enough vibration in the tube to knock off the deposit.

None of these methods is entirely satisfactory, and the operating engineer must choose the one best suited to his case. Experiments have been made with a compound of saltpeter, which, it is claimed, will momentarily increase the temperature of the gases enough to burn the carbon deposit to ash, which can be blown out of the stack.

With hand operated jets, it is the usual practice to blow out the dust once in 24 hours, although with most fuels it is found that dust begins to collect on the tubes immediately after it is blown out, and that, at the end of 6 or 8 hours, the heating surfaces are again coated. This would indicate that you should blow out boilers at least every eight hours, but with hand blowers this would involve increased labor cost. For this reason the mechanical soot blower is a desirable equipment. It has the advantage that with it a large part of the boiler is blown out at once, so dust is not blown from one part to settle on another. On a test made on a 360 horse power B. & W. boiler in a large gas works, it was found that, by using the blower every six hours instead of once in 24, the average stack temperatures were reduced 110°, and the boiler efficiency increased about 4 per cent, with a saving of 6 hours labor of one man.

Mechanical blowers are expensive to install but are worth considering where fine bituminous fuel is used, or where extra labor is required for hand blowing.

In using any blower, it must be supplied with absolutely dry or slightly superheated steam, at the highest obtainable pressure. Long runs of small pipe must be avoided, and the lines to them should be well drained. If wet steam is blown against the tubes it will make a pasty carbon formation that will bake on the tubes.

Baffling.—Boiler baffles are designed to so deflect the gases as to bring them into contact with all the heating surface, without too greatly obstructing the gas passages. Standard baffles are generally efficient for the type of boilers for which they are designed, and it is not often advisable to change the baffling without consulting the manufacturer. All brick baffles, but especially the vertical type, are likely to prove inefficient if they are not perfectly tight. It is considered good practice to cover vertical baffling with plastic fireclay cement, which fills the openings around the tubes and between the tile. This is sometimes done with horizontal baffles to insure their being tight, but it is not so important. For horizontal baffling there is usually a choice for the lower baffle between C tiles which enclose the tubes or T tiles which rest on top, leaving the lower half of the tube exposed. C tile is recommended where bituminous and semi-bituminous coals are burned in furnaces having insufficient com-

bustion space. They are higher in cost and more expensive to maintain than T tile, as they burn off and drop out of place. With a furnace properly designed for bituminous fuels, and with anthracite coal, slightly better efficiency has been obtained in comparative tests, when using T tile.

Types of Grates.—Grates are divided into three classes—stationary, shaking and mechanical stokers. Stationary grates are the oldest form and in most general use. They are of cast iron, with air spaces of usually slot or cone shaped holes. The percentage of air space in any grate varies with the fuel and nature of the draught, but they should be designed to give greatest possible percentage of air space without the openings being wide enough to weaken the casting or allow good fuel to drop through. A grate is an additional resistance to the passage of air through the fuel bed, and this resistance should be reduced as much as possible.

Stationary grates are low in cost, and can be easily replaced when burned out, and have comparatively long life.

Shaking grates are higher in first cost and likely to burn out more rapidly, as the bars are in contact with hot fuel when fires are shaken down. They are a decided advantage with bituminous coals which clinker badly, as the clinker can be broken up and shaken into the ash pit without the frequent use of a slice bar. This usually means a saving in labor, less frequent opening of the fire door, with consequently less cold air taken into the furnace, and a better distribution of air to the fire. With small size anthracite and other high ash coals the dumping grate may be used to advantage, as time will be saved in cleaning fires. If the ash pits are so arranged that they can be dumped into conveyor or cars, there is little doubt as to the desirability of shaking and dumping grates, but if the ash pits must be drawn through the doors, dumping grates are of doubtful value though shaking grates may be used with advantage.

Stokers.—Mechanical stokers can often be installed to advantage, if plant conditions are right.

It is claimed that stoker fired furnaces give the following advantages over hand fired:

- (a) Better maintained economy of operation.
- (b) Less labor required.
- (c) Smokeless operation with high volatile coals.
- (d) Better control of steam pressure under variable loads.
- (e) Better economy at high overload capacities.

As high efficiency has been obtained with good hand firing as with any stoker, and it is the general opinion of boiler engineers that, except with high volatile bituminous coals, a first-class fireman can obtain slightly better results, with a properly designed furnace, than can be obtained with a stoker. The reason for this is obvious, when we consider that a first class fireman does all that a stoker does, and in addition gives what

no machine can give, the benefit of his expert knowledge. Stokers claim to give uniformity of feed of coal, proper air supply to the fuel bed, and admit no air over the fire and automatically clean the fire. Various types of stokers do these to a greater or less extent, but a first-class fireman can improve on a stoker in fuel distribution and air supply, which are the most important items for efficiency, and he can keep cold air losses and cleaning losses to a minimum. Please note that we say "first-class fireman"; for it is on this term that most of the following depends. A really first class fireman, a man who understands combustion and has the will and ability to use his knowledge, is about as rare as the Dodo. Fairly good firemen, who can be depended on to do as they are told, are seldom found in the ordinary fireroom, because they are in demand for special testing work at higher wages, and because men of that caliber soon graduate from the fireroom into the engine room. Fireroom labor is usually classed as little above common labor, and the men paid accordingly, and the difference between good and bad hand firing is in the amount of physical labor expended and in the amount of knowledge and headwork used in doing it.

The question of the relative importance of labor and fuel costs is well worth considering, and the saving that can be effected by an increase of one pound of water evaporated per pound of coal will be surprisingly great compared with the additional cost of labor necessary to keep an efficient and contented fireroom force.

Mechanical stokers are rapidly taking the place of hand fired grates, in spite of their high cost, because they do, as a rule, give better efficiency in daily operation.

It is doubtful if stoker installations effect much saving boiler room labor unless coal is fed by gravity from storage to the stoker hopper. An average fireman can efficiently handle about 2,000 pounds of coal per hour, with hand-fired boilers, equivalent to 400 to 700 boiler horse power. A stoker fireman should be able to handle efficiently from 1,500 to 2,500-horse power and even as high as 3,000 horsepower of stokers, if he does not have to handle his coal and ashes.

It is claimed that stokers can be operated smokelessly, even at high overload, with all coals, provided they are set in properly designed furnaces. But it is also true that hand fired furnaces can be operated practically smokelessly with all coals except those containing more than 25 per cent volatile. Smokeless operation is entirely a question of complete combustion of the volatile gases from the coal, at a temperature above the ignition point, which for carbon monoxide is about 1,200 degrees F., and it is, therefore, mainly a question of proper furnace design. The reason for obtaining more continuously smokeless combustion with stokers is that the coal is fed evenly and a small quantity at a time, the gases being distilled slowly.

(E) *Furnaces*.—Combustion is the chemical union

of the combustible matter in a fuel with the oxygen of the air. Theoretically, it is a simple process, being only necessary to bring each atom of combustible matter into contact with the proper quantity of oxygen to produce combustion to CO_2 and water vapor. Practically, it is impossible in any boiler furnace to bring about this intimate mixture, and in commercial boiler practice either insufficient air is supplied and the combustible not completely burned, unburned CO and hydro-carbons escaping from the stack; or there is a large excess of air supplied and part of the heat generated by combustion, instead of doing useful work, is lost in heating the excess air.

The best modern practice requires that the furnace be supplied with at least 50 per cent more air than theoretically required for complete combustion, as losses due to excess air are, within limits, less than those due to incomplete combustion. The loss due to even a small percentage of CO will be realized when it is remembered that one pound of carbon burned to CO_2 gives 14,544 B. T. U.'s, and burning to CO it gives only 4,325 B. T. U.'s.

Perfect furnace operation with the theoretically correct amount of air would give flue gases containing over 20 per cent CO_2 and no CO, but the best designed bituminous coal furnaces do not give over 15 per cent CO_2 and seldom more than 12 per cent continuously, with a trace of CO, and consequently are being supplied with between 50 and 100 per cent excess air. The reasons for this apparently large excess amount of air are as follows:

(a) Difficulty in getting a uniform distribution of air to all parts of the fuel bed.

(b) Uneven distribution of fuel on the grate, and unequal resistance of different parts of the fuel bed to passage of air.

(c) Variable rates at which the gases from fresh coal are distilled, due to hand firing of fresh coal in varying quantities; or, with stokers, sliding of coal from hopper to grate. The supply of air being practically constant, a moderate excess at times when no gases are being given off, would be insufficient for complete combustion during coaling. Hence the necessity for excess air and the strongest argument in favor of coaling a fire light and often.

(d) The practical impossibility of providing any effective means of intimately mixing the gases and air above the fire. Many devices partly accomplish this, but the air and gas apparently have no strong affinity for each other and there is a tendency towards stratification.

It is impossible to evolve a furnace that will even approach theoretical perfection, but it should be the object of every engineer to design and operate furnaces to approach as nearly as possible to ideal conditions. Table No. 1 gives the loss due to excess air with different stack temperatures, and Table No. 2 the loss due to various percentages of CO for different percentages of CO_2 in the flue gases.

As seen from Table 1, it is impossible to prevent loss from heat carried away in the chimney gases, even if complete combustion with the theoretical amount of air could be obtained. In actual operation this loss can seldom be reduced below 15 per cent and is usually 20 per cent or more; but for any stack temperature the lower the excess air the less the loss. Stack temperatures usually depend more on the physical condition of the boiler and on the rate of steam production than on furnace conditions.

TABLE 1—TEMPERATURE OF CHIMNEY GASES—DEGREES FAHRENHEIT.

	300°	350°	400°	450°	500°	550°	600°	650°
12	750	905	1,060	1,116	1,370	1,528	1,683	1,840
*	5.2	6.5	7.3	8.7	9.5	10.5	11.6	12.7
15	865	1,112	1,305	1,498	1,679	1,880	2,072	2,262
	6.0	7.6	9.1	10.3	11.6	13.0	14.3	15.6
18	1,004	1,321	1,550	1,778	2,010	2,235	2,460	2,692
	7.2	9.1	10.7	12.2	13.9	15.4	17.0	17.9
21	1,266	1,530	1,785	2,060	2,320	2,582	2,846	3,118
	8.7	10.5	12.3	14.2	16.0	17.8	19.5	21.0
24	1,440	1,740	2,040	2,340	2,640	2,940	3,240	3,540
	9.9	12.0	14.0	16.1	18.2	20.3	22.4	24.4
27	1,611	1,950	2,281	2,620	2,958	3,291	3,628	3,962
	11.1	13.5	15.7	18.1	20.4	22.7	25.0	27.4
30	1,785	2,160	2,530	2,900	3,270	3,641	4,016	4,396
	12.4	14.9	17.4	20.0	22.6	25.0	27.8	30.4
33	1,957	2,362	2,779	3,180	3,589	4,000	4,405	4,820
	13.5	16.3	19.2	22.0	24.7	27.6	30.5	33.2
36	2,130	2,579	3,020	3,461	3,910	4,350	4,798	5,290
	14.7	17.8	20.8	23.9	27.0	30.0	33.0	36.6
39	2,300	2,781	3,261	3,743	4,220	4,700	5,180	5,670
	15.9	19.2	22.5	25.8	29.2	32.4	35.7	39.0
42	2,479	2,999	3,508	4,023	4,540	5,052	5,570	6,100
	17.1	20.6	24.7	27.7	31.3	34.8	39.4	42.0

*Theoretical requirement.

Upper figures in each double line give the loss in B. T. U.'s per pound of combustible; lower figures the per cent loss, assuming a calorific value of 14,500 B. T. U.'s per pound of combustible.

TABLE 2—PER CENT OF CO₂ IN THE FLUE GAS BY VOLUME.

	6.	8.	10.	12.	14.	16.
	328	248	199	168	144	126
0.2	2.2	1.7	1.3	1.1	1.0	0.8
	635	484	390	327	282	248
0.4	4.3	3.3	2.6	2.2	1.9	1.7
	925	709	575	474	417	367
0.6	6.3	4.8	3.9	3.2	2.8	2.5
	1,192	923	750	635	549	495
0.8	8.1	6.3	5.1	4.3	3.7	3.4
	1,494	1,128	923	780	676	596
1.0	10.2	7.7	6.3	5.3	4.6	4.1
	1,690	1,321	1,085	923	801	708
1.2	11.5	9.0	7.4	6.3	5.4	4.8
	1,920	1,512	1,248	1,061	924	819
1.4	13.1	10.3	8.5	7.2	6.3	5.6
	2,104	1,693	1,400	1,193	1,040	924
1.6	14.3	11.5	9.5	8.1	7.1	6.4
	2,340	1,865	1,549	1,321	1,151	1,025
1.8	16.0	12.7	10.5	9.0	7.8	7.0
	2,537	2,030	1,690	1,450	1,270	1,129
2.0	17.2	13.8	11.5	9.9	8.6	7.7

Upper figures in each double line give the loss in B. T. U.'s per pound of combustible, and lower figures the loss in per cent, assuming a calorific value of 14,500 B. T. U.'s per pound of combustible.

Furnace Design.—An important question is that of the best design of furnace for the fuel available.

Considering the furnace as distinct from the boiler, grates and draught system, it is efficient when stack gas analyses show a continuous high percentage of CO₂, with maximum of CO. Flue gas analyses are the best tests of furnace efficiency, but low CO₂ or high CO is not always an indication of a poorly designed

furnace. If flue gas analyses are to be depended on to determine the efficiency of furnace design, care must be taken to see that the following conditions are complied with.

(a) That samples taken represent the average of the stack gases. Samples should be taken from the last pass of the boiler and also from the first pass. A marked difference in the analyses of these two points will usually indicate air leakage in the setting.

(b) That samples are correctly analyzed, using solutions of the proper strength. This is especially important in determining CO, as it is absorbed with difficulty.

(c) That fire conditions are good, that coal is fed in small quantities and well spread, and that there are no holes in the fire. Heavy firing means high CO, and uneven fires excess air.

(d) That the brickwork of the setting is air-tight. This can usually be determined by testing with a candle flame, but some settings are so thin and porous that they allow infiltration of air which cannot be detected. Such a condition can usually be discovered by taking samples from different points of the boiler, and can best be stopped by painting or cementing the settings.

(e) That the amount of air supplied to the fire is nearly correct. This will vary for different grades of coal and fire conditions, but can be determined by finding the differential pressure through the fuel bed, and making a gas analysis. By making a preliminary set of analyses and noting the differential pressure at the time the CO₂ in the gases is a maximum and the CO a minimum, the correct intensity of draught can be determined.

With hand firing, and bituminous coal, if an average of 10 per cent of CO₂ with less than 0.5 of a per cent of the CO can be maintained, and the stack gives off little black smoke, it can be assumed that the furnace is efficient for the fuel used.

Furnaces are usually inefficient because they do not provide sufficient space for complete combustion of the gases from the fuel before they are cooled below their ignition point, or because the gas passages are so short and direct that the air and gases are not intimately mixed.

The first fault can usually be remedied by:

(a) Lowering the grates to give more space between the fire and the tubes or shell of the boiler. This will involve changes in the boiler front and lowering the floor of the boiler room.

(b) Raising the boiler and allowing the grates to remain in their old position. This will accomplish the same results as lowering the grates, and is often the cheaper and better method.

(c) By installing a Dutch oven or extension furnace, wing wall, or other furnace that gives increased combustion space, and longer gas passages. Furnaces of this type are usually expensive to construct and to maintain, and are of doubtful value except for high

volatile fuels, extensively used for small sizes of anthracite coal.

(d) By the installation of steam jets or other form of secondary air supply. Most of these devices are of doubtful value.

(e) In the case of return tubular and horizontally baffled water tube boilers, by the use of special baffle walls back of the bridge wall; or checker work arranged to break up the flow of gases and increase the combustion chamber temperature. Devices of this kind may prove effective, but usually burn out or fill up with soot after a few weeks' operation.

PRODUCTION OF ALUMINUM ORE IN 1913.

The demand for aluminum in the United States in 1913 showed a steady and rapid growth, according to W. C. Phalen of the United States Geological Survey. This resulted in a marked increase in the production of bauxite or aluminum ore, the output of which, according to final Survey figures, was 210,241 long tons, valued at \$997,698, an increase of 50,376 long tons, or 31.5 per cent and \$228,766 or 29.8 per cent, respectively, over the figures for 1912. This growth of the aluminum industry has been marked by healthy expansions and improvements in existing plants, the commencement of work at a new plant in the spring of 1914, and progress in the work on new power sites where largely increased hydro-electric power for use in the reduction of the metal will be in operation during the next few years.

The states which produced bauxite were, as usual, Alabama, Arkansas, Georgia, and Tennessee. Arkansas led in 1913, its output exceeding that of the previous year. The ore mined in that state came from both Saline and Pulaski counties. The production in Tennessee increased substantially. The ore mined in this state came from the Mission Ridge deposits near Chattanooga, and from the new mine of the National Bauxite Company near Keensburg, Carter County. The production in both Georgia and Alabama declined. In the former state the decline was slight, but in Alabama it was considerable. In Georgia ore was mined near Hall's Station, Bartow County; near Hermitage, Floyd County, and near McIntyre, Wilkinson County. Considerable prospecting and development work was done in the vicinity of Rome, Floyd County. In Alabama ore came from the vicinity of Rock Run, Cherokee County.

The average price of bauxite per long ton at the mine for 1913 was \$4.75, which differed by only a few cents from the prices recorded for the three previous years. There was more aluminum consumed in the United States in 1913 than in 1912, but the figures showing this consumption can not be published at the present time, as the import figures are not yet available.

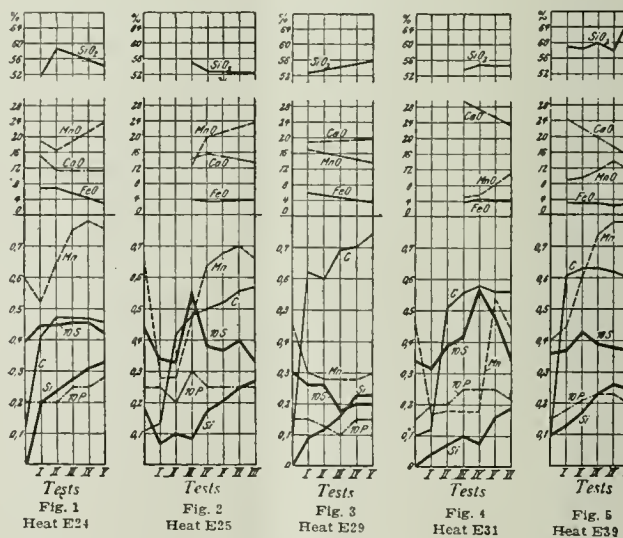
THE ACID ELECTRIC FURNACE PROCESS.*

Experiments with an acid hearth in electric furnace work have been vigorously carried on during recent years in Europe. This is particularly true of the plant of the Lindenberg Steel Company at Remscheid, concerning which an article was published in *The Iron Age* of June 5, 1913. In further reference to this subject an article has just appeared in *Stahl und Eisen* by Dr. A. Müller, giving the results obtained with an acid lined 3-ton Girod furnace at Gutehoffnungshütte.

TABLE I—CHEMICAL COMPOSITION OF THE ACID AND BASIC FURNACE MATERIALS.

Constituent.	Furnace hearth—		Acid walls—	
	Before the test.	After 27	Before the test.	After 27
	Basic,	Acid,	Basic,	Acid,
	per cent.	per cent.	per cent.	per cent.
SiO ₂	5.72	80.50	64.60	95.30
CaO	46.50	4.30	12.90	1.85
MgO	27.60	1.91	2.90	Trace
Al ₂ O ₃	1.46	3.08	2.65	0.58
Fe ₂ O ₃	1.85	.38	.43	0.57
FeO	0.99	1.16	1.93	0.26
MnO	0.40	.27	12.05	0.19
P ₂ O ₅	0.09	0.02	0.02	0.08
Carbon	8.60	7.75	1.20	...
Loss on ignition	14.35	7.80	...	...

The hearth was rammed in place and consisted of 80 per cent old silica bricks, 6 per cent fire clay, and 14 per cent tar. It reached to the upper edge of the six steel hearth pole pieces. Table I gives analyses of the hearth and siliac brick walls before and after the 27 test heats.



The great change that takes place is clearly evident. The carbon of the hearth is reduced, which occurs during the first few heats, and leads to an excessive and undesired carburizing of the bath. With an acid hearth it also brings about considerable reduction of silica, so that the first heat is too high in silicon to be suitable for all purposes. The first heat therefore should be used more or less for a thorough heating of the hearth, and the steel used for rolling or forging if thought desirable.

*From *The Iron Age*.

TABLE 2—DETAILS OF SEVERAL ACID HEATS.

Method of Working	Test No.	C	Mn	P	S	Si
Heat E 24:						
Open-hearth heat 324.....		0.12	0.60	0.020	0.040	Traces
18 kg. petrolcum coke.....	1	0.42	0.52	0.020	0.045	0.20
10 kg. ferromanganese.....	2	0.47	0.61	0.020	0.045	0.24
12 kg. ferromanganese.....	3	0.47	0.75	0.025	0.046	0.28
	4	0.47	0.78	0.025	0.046	0.31
	5	0.46	0.76	0.028	0.043	0.33
Heat E 25:						
Open-hearth heat 330.....		0.11	0.66	0.025	0.044	0.18
20 kg. ore.....	1	0.13	0.28	0.025	0.034	0.07
20 kg. petrol. coke or old electrodes.....	2	0.42	0.28	0.020	0.033	0.10
20 kg. ferromanganese.....	3	0.48	0.40	0.030	0.053	0.09
10 kg. ferromanganese.....	4	0.50	0.64	0.025	0.038	0.18
3 kg. ferromanganese.....	5	0.52	0.68	0.025	0.037	0.21
	6	0.56	0.70	0.025	0.040	0.25
	7	0.57	0.66	0.025	0.034	0.27
Heat E 29:						
Open-hearth heat 360.....		0.09	0.46	0.015	0.030	Traces
28 kg. petrol. coke.....	1	0.62	0.30	0.015	0.026	0.09
3 shovels sand.....	2	0.60	0.28	0.013	0.026	0.12
Coke to reduce MnO in slag	3	0.69	0.28	0.010	0.018	0.16
	4	0.70	0.28	0.015	0.020	0.23
	5	0.74	0.30	0.015	0.020	0.23
Heat E 31:						
Open-hearth heat 383.....		0.10	0.45	0.015	0.034	Traces
60 kg. ore.....	1	0.12	0.17	0.020	0.032	0.04
22 kg. coke or electrodes.....	2	0.51	0.18	0.020	0.039	0.07
(Test is red short).....	3	0.56	0.18	0.025	0.042	0.10
(Test is red short).....	4	0.58	0.18	0.025	0.057	0.08
20 kg. ferromanganese.....	5	0.56	0.54	0.025	0.048	0.16
	6	0.56	0.44	0.022	0.035	0.19
Heat E 39:						
Open-hearth charge.....		0.09	0.40	0.015	0.036	0.10
24 kg. petrol. coke.....	1	0.61	0.44	0.018	0.037	0.13
10 kg. ferromanganese.....	2	0.63	0.60	0.021	0.043	0.17
15 kg. FeMn, 3 shovels sand	3	0.63	0.74	0.023	0.039	0.23
4 shovels sand.....	4	0.62	0.78	0.023	0.038	0.26
	5	0.60	0.78	0.020	0.037	0.25

Tables 2 and 3 show the metallurgical course of five heats, giving analyses of metal and slag, and these results are shown in diagram form in Figs. 1 to 5. The reduction of silica is the most important of all the reactions in the acid furnace, and from the results given four phases of this reduction can be separated:

1. Constant and almost exclusive reduction from the acid hearth and walls. The silicon reduction under normal conditions is mostly from these sources, as for instance in heat E 25.

2. Reduction of silica by increasing the silica con-

tents of the slag. This can be seen in heats E 29 and E 39 where the silicon in the bath rises rapidly following an addition of sand to the slag. The slags are notwithstanding increased in silica to 55.80 per cent and 66.27 per cent, respectively; they became difficultly fusible and required more heat.

3. Reduction of silica by increasing the temperature of the slag. An increase in the slag temperature is readily brought about in the electric furnace, and renewed silica reduction sets in. This is seen with heat E 24, where the silica in the slag dropped at one time from 58.80 per cent to 54.40 per cent, while the silicon in the bath increased about 0.1 per cent.

4. Reduction by means of carbon. At a certain temperature the free silica in the slag is reduced, the silicon entering the bath. This reaction is clearly seen during the carburizing period, as, for instance, with E 24, where the silicon rises to 0.20 per cent, while the carbon increases at the same time by 0.30 per cent. All these reactions are more energetic the higher the temperature of the bath and slag. The reduction from the lining is particularly active with a newly lined furnace, but decreases comparatively quickly, as is readily understood from the analyses given in Table 1. As soon as this reduction is quieter the silicon of the bath can be somewhat regulated by the temperature and composition of the slag, for the ability to reduce silicon from the slag depends on these two factors.

We see, also, that reactions in the acid electric furnace are more vigorous than in the acid open hearth, and on the whole more active than in the crucible. This reduction of silicon is of benefit economically as well as in regard to quality, for no addition of ferro-silicon is needed. The silicon reduced during the course of the heat in the body of the steel gives a characteristic quietness to steel deoxidized in the acid electric furnace, and according to Thallner, Geilenkirchen, and Eilander ought to have a particularly good influence on the size of the crystals and structure of the steel. Certainly silicon introduced into the bath in this

TABLE 3—SLAG ANALYSES OF SEVERAL ACID HEATS.

Heat	Test No.	SiO ₂	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	S	P ₂ O ₅	O of base O of acid
E 24.....	1	51.50	15.30	3.80	2.60		6.95	18.85	0.25	0.01	
	2	58.80	11.40	4.30	2.14		6.85	16.30	0.27	0.03	
	5	54.40	11.50	5.20	1.72		3.35	23.55	0.29	0.03	
Oxidizing slag.....	..	39.02	5.80	1.50	1.92	2.15	23.80	25.41	0.15	0.20	
	3	54.84	14.50				3.85	12.66	0.20		
E 25.....	5	52.70	15.80				3.60	20.15	0.12		
	7	52.60	13.70	3.20	1.52		3.85	23.70	0.13	0.12	
E 29.....	1	52.50	18.75	2.90	1.36		5.80	16.70	0.11	0.05	
	5	55.80	19.60	4.02	2.02		3.55	13.85	0.03	0.03	1-3
Oxidizing slag.....	..	45.10	5.35	2.10	1.75	2.30	23.65	19.30	0.40	Traces	1-2
	3	53.50	29.60	3.10	1.49	0.43	3.60	4.95	0.37	Traces	
E 31.....	4	55.20					4.35	5.70			
	5	54.20					4.25	8.35			
	6	54.20	23.20	3.05	1.86	0.35	4.05	11.15	0.40	Traces	2-3
E 39.....	1	58.83	24.29	2.40	1.75	0.29	3.07	8.93	0.39	Traces	
	2	58.54					2.96	9.59			
	3	59.78					3.08	11.45			
	4	57.92					2.58	13.79			
	5	66.27	15.26	2.03	0.15		2.81	11.68	0.51		1-4

way is preferable and has a better action than silicon added as ferrosilicon, which must be mechanically mixed with the bath, and often leaves deoxidation products that do not separate from the metal.

While the silicon plays the chief metallurgical rôle the behavior and the amount of the sulphur is of great importance. The diagrams show that the sulphur is subject to considerable change during the melting, but in most cases the final analysis shows a decrease. Desulphurization can be noticed to some extent during the oxidation period, the sulphur probably escaping as SO_2 . This is noticeable with heat E 25. During the reduction period a new desulphurizing influence is active to an extent sufficient to keep the sulphur down to, at least, the original percentage. The petroleum coke for addition to the bath carries in considerable sulphur; for instance, in heat E 29 the 28 kg. of coke adds about 0.01 per cent sulphur to the bath. As this is again separated from the bath we can very properly speak of desulphurization in the acid furnace. It is probable that this is effected by the formation of calcium sulphide and sulphide of silicon, SiS_2 , as in the basic process.

An acid slag must be used to preserve the acid hearth and walls. With cold charges the impurities form a slag with oxide of iron, but with liquid charges slag making materials must be thrown in. As in the basic electric furnace process the slags can be separated according to the method of working into oxidation and deoxidation slags. The first is an iron-manganese-silicate slag similar to the ordinary acid open-hearth slag, while the latter can only exist in the real reducing atmosphere of the electric furnace. It can be produced by charging, on to the clean surface of the bath, 75 per cent crushed silica bricks and 25 per cent burnt lime, which mixture will soon be liquid without any addition of fluorspar. This produces a totally different acid slag, which also suffers considerable changes during the course of the heat.

For the proper carrying out of a correct slag practice, great care is necessary so as to have a good final slag that will allow good refining, and not cause too great injury to the acid hearth and lining. This question is gone into in some detail. The proper basicity of the slag is best obtained with lime and magnesia and the lime contents are best held between 15 and 20 per cent. The magnesia should mostly vary from 2 to 5 per cent. If greater basicity is desired then it should be produced with oxide of manganese, the most suitable amount being 10 to 15 per cent. Finely crushed ferromanganese can be added to the slag to produce this oxide. If it rises too high a small addition of petroleum coke will quickly reduce it. Table 3 gives typical analyses of permissible slags.

There can be no doubt that in plants where a raw material, sufficiently low phosphorus and sulphur, can be obtained refining with the acid electric process is to be preferred to the basic process—particularly when the highest grades of steel do not have to be made

nor the sulphur and phosphorus reduced to a minimum. Without exerting any special care a series of such steels made from open-hearth material gave a phosphorus of 0.02 per cent, and a sulphur of 0.035 per cent. These small percentages exerted no harmful influence on the physical properties of the steels produced, which were not supposed to be of the highest quality. Much more important is the care in working, the melting and finishing of the charge, good slag practice and correct temperatures.

Thallner attributes special influence to the temperatures on the internal structure and quality of the metal. Good melting in the acid furnace is by no means easy, and of course good, carefully made, basic steel is better than poorly made acid material. Extensive practical experience and metallurgical knowledge is necessary to get the best results and have a product that exceeds good basic electric steel. Experience is to the effect that the higher phosphorus and sulphur contents of the acid steel do not exert a harmful influence on the physical properties, and so it may be assumed that both kinds of steel, with otherwise equal conditions, are equal in quality. The acid process is more economical than the basic, under the conditions given above, and is therefore to be preferred.

SUMMARY OF ADVANTAGES.

The advantages may be summed up as follows:

1. Smaller current consumption through shorter melting time, due to the shortening or absence of the oxidation period. This period is only necessary if the final steel is to have less carbon or manganese than the charge.
2. Saving in deoxidizing agents. All the silicon comes from the lining or the slag. As the deoxidation is more active and continuous than in the basic process the melting time can be further shortened.
3. Important lessening of the repair and relining costs, as the acid material is much cheaper than dolomite or magnesite.
4. Reduced cost of materials for additions. The final acid slag can be profitably recharged in subsequent heats.

The acid electric furnace process offers therefore important economic advantages, where suitable raw material is available for the charges, and where the highest and special grades of steel are not desired.

In the calendar year 1912 there were invoiced at the Para consulate for export to the United States shipments of crude rubber having a declared value of \$12,540,860, as against \$19,453,689 in the calendar year 1912. Shipments were heaviest in the March quarter, the declared exports for that period totaling \$5,198,119; in the June quarter the invoices aggregated \$2,528,159; in the September quarter, \$2,058,819; and in the closing three months of the year, \$2,755,763.

ELECTRIC FURNACES FOR STEEL MAKING.*

By E. B. CLARK.†

The engineering societies and the technical publications have received so many contributions to the general subject of electric furnaces that one feels a natural reluctance in attempting to add anything to the literature of the subject. It is to be noted, however, that many of the contributions have been made by men interested in the exploitation of some certain type of furnace. It is quite to be expected that such contributions should be biased, not intentionally, perhaps, but still to a sufficient extent to place all such discussions under the ban of suspicion.

The intending user of an electric furnace wishes dependable answers to two questions:

First—How will an electric furnace compare with some other apparatus for producing or refining steel as to quality of output and cost of operation?

Second—Assuming the wisdom of an electric furnace installation, what is the best type of furnace, and what size of unit is proper?

Most of the available literature upon these subjects is of a theoretical nature. Information from a practical standpoint will generally be acceptable, but when one is actually a user of electric furnaces in the commercial production of steel he does not find a great deal to say. After all, this is not a surprising fact, for the electric furnace does not offer anything radically new in the production or refining of steel. Its use is generally contemplated for a purpose where steel may be made or refined either in an electric furnace, a crucible furnace, a Bessemer converter, or an open-hearth furnace.

The crucible furnace enables one to make accurate alloy mixtures of high quality without contamination from gases or furnace linings. Practically no refining can be done and therefore high grade materials must be used for the mixture. By the law of supply and demand, the price of pure materials for use in crucible furnaces will be higher where the crucible process is employed to a considerable extent. The electric furnace will produce steel of the same degree of purity as a crucible furnace, and the possibility of refining in an electric furnace makes possible the use of less pure materials. This is an advantage for the electric furnace, and, at the same time, an advantage for the crucible furnace, because the demand for the high grade materials necessary in the crucible process is reduced by each additional electric furnace installation and therefore the price of the charge for the crucible furnace is reduced. This is especially true as applied to the small crucible furnaces used in foundry practice, which require low-phosphorus steel punchings for their successful operation.

The small Bessemer converter, or Tropenas vessel, is capable of producing hot steel in small units quickly. It does not permit of refining, however, and therefore necessitates the use of low phosphorus and low sulphur pig iron which must be pre-melted in a cupola, using high grade coke. The losses are severe and the steel is not free from oxides and occluded gases. The electric furnace will produce steel just as hot as the small Bessemer vessel, but free from oxides and occluded gases. However, the electric furnace requires scrap for charging rather than pig iron, so if only pig iron is available at commercially desirable figures, the pig must be converted into steel before charging into the electric furnace.

The open-hearth furnace will produce, from pig and scrap, steel of a fairly high degree of purity and of fairly high temperature. The electric furnace will do the same thing (except that the use of a large percentage of pig is not desirable) and is capable of producing purer and hotter steel than is the open-hearth under usual operating conditions.

Summarizing these general observations, it may be said that for the alloying of steels the electric furnace offers nothing that the crucible furnace does not; for the production of very hot steel the electric furnace offers nothing that the Bessemer converter does not; and, metallurgically speaking, the electric furnace offers nothing that the open-hearth does not. It is a fact, however, and this is the important fact, that the electric furnace combines in itself certain advantages of all three of the other processes mentioned. On the other hand, it is seldom that one wishes to secure the advantages of all these other three processes combined in one. Generally, a certain object is in view by the intending user of an electric furnace or some other form of apparatus for producing steel. Of course, broad generalities will not solve this problem. The cost of production is the final answer from a commercial standpoint, and this depends not only upon the market for the intended output, but upon the available supply of steel making materials, and upon the availability of a satisfactory and sufficient cheap source of electric power. In passing it might be observed that this question of electric power supply is generally not so serious as might at first appear. In the first place, there are many locations where a sufficient amount of fairly cheap electric power may be purchased; and in the second place, the item of power is not often of supreme importance.

There are other elements entering into the production of electrically refined steel which have a far greater influence on the cost of production than is generally credited. The most important of these is experience. It should be understood clearly that the electric furnace is a more delicate apparatus than any of the other three furnaces mentioned. It is more difficult to handle and its operation offers more likelihood of mishaps. Electric furnace operation has not yet been re-

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†President, Buchanan Electric Steel Co., Buchanan, Mich.

duced to standard practice. Melters familiar with its operation are scarce and difficult to find.

To attempt an answer as to what type of furnace is best is as unsatisfactory as to make general comparisons between electric furnaces and other furnaces. If we could accept at face value the statements of a number of men interested in the development of certain electric furnaces, we could easily believe that as soon as a foundryman had installed an electric furnace (provided he installed the right one) his troubles would be at an end. As a matter of fact, he is apt to find that they are just beginning. In the first place, unless the design of the furnace has been thoroughly tried out in practice, it will certainly have to be modified considerably from the designer's ideas. In the second place, the user will certainly find the furnace to be a more delicate piece of apparatus than he had anticipated. He will find that while he can make steel of a very high quality, he can also make, without difficulty, much steel of a very low quality. If there are in the society some men who have been using electric furnaces for the production of castings or special steels, they will have no difficulty in recognizing these remarks as coming from one who has also had such experience. It so happens that the speaker's experience has embraced not only a study in this country and Europe of the design and operation of a number of different types of furnaces, but has embraced the actual operation of two typical types of furnaces for the production of steel castings. The investigation as to which general type of furnace is best led in my case, as in that of most others, to much confusion of ideas. It is so evident that each type has certain advantages and disadvantages, and so impossible accurately to gauge the proper importance of the various advantages and disadvantages, that one cannot reach a conclusion as to which type of furnace is best, with confidence in his conclusion. Perhaps the only way to learn is to try them all. As a matter of fact, the speaker has already tried two, and feels that he has not yet decided the question.

We have operated two furnaces of one to one and a half tons capacity each, of the surface-arc type. This general type is best exemplified by the Stassano furnace, the general construction of which is well known. Our furnaces use three-phase power and the arcs are maintained above the surface of the bath. They are lined with magnesite brick, which, of course, while a high refractory, is quite susceptible to damage by sudden heat changes. Very hot and very good steel has been produced in these furnaces. The cost of repairs has been rather high, due to necessity for relining rather frequently. We have found that linings last, under proper treatment, about forty to fifty heats, though we feel that some changes in methods of construction would increase the number of heats per lining and, therefore, decrease this item of cost very considerably. The labor cost on these furnaces has been found to be rather high, but this is principally due to

the small capacity of the furnace. The power costs have not been high when the furnace has been operated continuously, even despite the small capacity of the charge. Where commercial conditions have made it necessary to permit considerable time to intervene between heats, the power consumption has been increased, due to the necessity of keeping the furnace fairly hot between heats. Experience in operation, however, has made it possible to reduce this item of expense far below what was originally believed possible. Even where the furnace is operated on day turn only and kept hot over night with current, the power consumption was surprisingly low for so small a furnace. Electrode costs have been quite reasonable.

Summing up, it may be stated that the operation of these furnaces has been quite satisfactory, as regards quality of output, reliability of operation and cost of production, when the size of the furnace is taken into consideration. Two furnaces should be used alternately, so that ample time can be allowed for relining, without interfering with the continuing supply of hot metal.

The increasing demand for hot metal for foundry purposes led us to consider the installation of additional metal-producing capacity. We consider that the type of furnace which has just been described is not suitable for units above from two to two and a half tons capacity, because of the increasing difficulty which probably would be experienced with linings in the larger sizes. As a furnace of approximately five tons capacity was necessary, we decided to install one of the submerged-arc type, represented by such furnaces as the Heroult and Girod. A Heroult furnace was put in and has been operated very satisfactorily. Power consumption has been less than in the smaller furnaces, but only by an amount which would be expected for the difference in size of the furnaces. As a matter of fact, claims for low power consumption by any furnace should be received skeptically. It is a fact that the power consumption of any electric furnace depends somewhat upon the efficiency of the furnace, but it also depends to a far greater extent upon the method of operating the furnace. The furnace efficiency depends upon the thoroughness of the heat insulation, for, after all, the only heat which is lost is that which escapes by radiation or conduction. That which goes out in the slag, or in the steel, depends not upon the efficiency of the furnace, but upon its mode of operation. Where a high degree of refining is necessary, slags must be taken off, at the cost of power consumption. Where the furnace must be operated with considerable time between heats, heat is escaping rapidly during that idle time. Where heats must be held in the furnace, or melted slowly, to meet a definite schedule, a high power consumption must be expected. For these reasons it appears that the claims for low power consumption of certain furnaces are practically valueless from an operating standpoint. The conditions of operation, rather than the type of furnace, are what

control the power consumption, though, of course, the construction of the furnace, as regards heat insulation, does have some influence.

In our five-ton Heroult furnace, we have found the cost of repairs to be lower than in the smaller furnaces. This is due to a considerable extent to the type of furnace, but our experience in the operation of electric furnaces has also helped in this respect. Furthermore, we have not yet reached our hoped-for results as to repairs. The labor costs are less on the larger furnace, as might be expected, partly because it is automatically controlled, and largely because of its increased output. To summarize our views upon the relative merits of the two types of furnaces, as based upon our own experience, I would say that we have found the surface-arc type to be a much better furnace than its critics would have one believe. On the other hand, we have found the submerged-arc type better for our purposes because of its larger capacity and lower cost of operation. It would not be fair, however, to ascribe the lower costs entirely to its type, for the capacity of a unit certainly has much to do with the lower cost. Where a foundry is, like ours, entirely dependent for its supply of hot metal upon the electric furnace, this type is better by reason of less necessity for lining repairs.

No attempt has been made here to give actual figures of operation. This is not due entirely to reluctance to publish our costs of production. As a matter of fact, the costs of production are so much dependent upon local conditions, such as quality of scrap available, continuity of operation and price of electric power, that results obtained in one installation, if used as a basis for other installations, may be most misleading. The predominating influences in this case are the commercial conditions surrounding each separate installation.

In conclusion, I wish to reiterate my statement that an intending user of an electric furnace may expect to learn much more about the furnace by his experience after he gets it than by the statements of someone who wishes to sell him a furnace.

A concession has been granted to a Norwegian company to operate pyrite deposits in the vicinity of Ballanghalvoen, in Ofoten. These deposits were first discovered in 1890; the sulphur content, however, being 33 per cent, with only 1 per cent copper, they were never operated, as the methods in vogue made the expense per ton too great for profit. This obstacle has been overcome, and the company was incorporated with 2,000,000 crowns (\$556,000) Norwegian and German capital. Large crushing and washing plants will be erected at the mines, the yearly production being figured as 100,000 tons salable product, together with 100 tons of copper ore.

PIG STEEL FROM ORE IN THE ELECTRIC FURNACE.*

In a paper of considerable length, presented at the February meeting in New York of the American Institute of Mining Engineers, Robert M. Keeney, Pittsburgh, Pa., of the U. S. Bureau of Mines, discusses the subject of "Pig Steel from Ore in the Electric Furnace." The term "pig steel" has been defined by Dr. J. W. Richards of Lehigh University as "a metal with 2.2 per cent or less of carbon, a very small amount of silicon and manganese, low in sulphur and phosphorus, and made directly from ore in the electric pig-iron furnace." In chemical composition it is steel. Important extracts from the paper are the following:

In this paper the writer does not advocate the production of pig steel from ore in the electric furnace as a competitor of the present method of steel production with pig iron as an intermediate step, but presents the general metallurgical side of such a process and its economical possibilities in regions where power is cheap, and fuel and reducing materials are expensive, as, for example, Sweden, California, British Columbia, and the western coast of South America. The field of the electric furnace in pig-iron manufacture is restricted to such areas, and possibly will never have great application even in favorable districts, because of the cheapness with which iron ore can be delivered from western coast deposits to furnaces upon the eastern coast of the United States on the completion of the Panama Canal. But when in these countries local demand for pig iron and steel is great enough, the electric furnace has an opportunity. In such cases, if steel is the desired final product, it seems more feasible and cheaper to produce as pure a product as possible—pig steel—for any subsequent refining operations, rather than pig iron. This would prove to be the case for two reasons:

1. As has been found to be the case at Heroult, Cal., Domnarfvet, and Trollhättan, a pig steel can be produced more cheaply in the electric shaft furnace than pig iron, because of the greater output per unit of electrical energy consumed.

2. Owing to the lower percentage of impurities in pig steel, 1 to 3 per cent, instead of 4 to 8 per cent in pig iron, a greater output can be obtained from the final refining furnace at a lower cost.

A process to produce efficiently a metal conforming to these requirements should satisfy the following conditions:

1. As the product in order to be a steel must not contain over 2.2 per cent carbon, it should be possible not only to keep the percentage of carbon in the metal below that amount, but should also be possible to regulate the carbon within reasonable limits, i. e., control the composition of the metal.

2. The product should contain percentages of silicon, phosphorus, and sulphur either below the limit set

*From The Iron Age.

by consumers of Bessemer and open-hearth steels, or at least low enough not to require prolonged refining in another furnace.

3. The loss of iron in the slag should not be excessive.

4. The furnace used must be adapted to continuous operation and the production of a large tonnage.

5. By the process it should be possible to produce pig steel at a greater profit than by existing methods.

Considering the possibility of the use of the electric furnace to satisfy these requirements:

1. As it is not necessary to introduce carbon for fuel in the electric furnace it is not necessary to have excess carbon in the charge beyond that needed for reduction, therefore no difficulty should be experienced in keeping the carbon of the product below 2.2 per cent; and it should be possible to regulate the carbon within reasonable limits.

2. The temperature of the electric furnace can be regulated by the power input, so that very basic slags can be used, which should result in slagging of silicon, phosphorus, and sulphur.

3. While the loss of iron in the slag with an electric furnace running on pig steel would probably be greater than in the case of pig iron, owing to the weaker reducing atmosphere of the pig-steel furnace, it should not be so excessive as to prohibit the use of such a process under favorable economic conditions.

4. The electric shaft furnace has been proved to be easily adapted to continuous operation for pig-iron production, and should operate more uniformly on pig steel than on pig iron because there is not the tendency for carbon to accumulate in the furnace.

5. In localities where electric-furnace pig iron can be produced at a profit, pig steel for further refining could be made at a profit if the market demand was for steel.

Some experimental work performed by the writer in 1911 under a Carnegie Research Scholarship of the Iron and Steel Institute of Great Britain and the work of others serve to show the metallurgical possibilities of the electric furnace for the production of pig steel from ore, and whether the process satisfies the five stated requirements. Five groups of experiments were made on the electric-furnace production of pig steel, arranged as below:

Group I. A series in which both limestone and coke were varied in the charge.

Group II. A series in which the amount of coke in the charge was varied, other components remaining constant.

Group III. A series in which the amount of limestone in the charge was varied, other components remaining constant.

Group IV. A series in which a part of the limestone was replaced by varying amount of fluorspar, other components remaining constant.

Group V. An experiment in which the furnace was

operated continuously rather than intermittently, as in the other experiments.

Mr. Keeney here presents the details of the effect on the composition of the pig steel of the various alterations in the charges in accordance with these experiments and furnishes numerous analyses of the product and the slags, the yields and the kilowatt-hours per gross ton of pig steel produced. Commenting on these he says:

Trouble was experienced at the Hardanger, Norway, electric pig-iron plant with coke as a reducing material. The failure of this plant has been assigned to the use of coke, because coke has a higher electrical conductivity than charcoal and hence not as much heat is generated by the resistance of the charge to the passage of the electric current. For this reason, trouble might be experienced, with a shaft furnace using coke as a reducing agent in the production of pig steel, but the problem will undoubtedly be solved eventually. The writer visited the Hardanger plant a few months before it was closed, and from observation of existing conditions does not believe the failure of the enterprise was entirely due to use of coke.

J. Crawford says that at Heroult, while difficulty was experienced with coke alone as a reducing material, "by adopting certain precautions in crushing the stock and feeding the same into the furnace I have operated on a mixture of 60 per cent coke and 40 per cent charcoal with a very fair degree of furnace efficiency. I believe that many of our coals which make a poor metallurgical coke for blast furnace use on account of their low crushing strength might be found to make a satisfactory fuel for electric furnace use."

The results at both Domnarfvet and Trollhättan indicate that pig steel can be made directly from ore in the electric shaft furnace. In these runs no attempt was made to produce a pig steel, but the product contained from 1 to 3 per cent carbon, as before stated. While it would undoubtedly be more difficult to regulate the carbon of the product in a shaft furnace operated continuously than in an intermittent hearth furnace, it could be done, but the regulation would not be so close.

Summarizing the results of the experiments he says as to carbon: 1. In producing pig steel containing from 0.25 to 1.50 per cent carbon for any particular furnace and basicity of charge, the carbon content of the pig steel can be regulated by varying the carbon in the charge. 2. An increase or decrease of lime in the charge causes a corresponding decrease or increase of carbon in the pig steel. 3. The use of fluorspar in excessive quantities causes a marked increase in the carburization of the pig steel. 4. The experiments of Neveu and Arnou indicate that the carbon of reduction may be supplied from coke, anthracite coal, or charcoal, and the charge may be fine, coarse, or briquetted. 5. The work at Domnarfvet and Trollhättan shows the possibility of keeping the carbon of the product below 2.2 per cent in an electric shaft furnace.

As to silicon the experiments show in general that the percentage of silicon in the pig steel can be kept at a low figure if desired, and that its regulation is not difficult.

The conclusions as to phosphorus, drawn from these results, are: 1. Increased carbon in the charge causes an increase of the percentage of phosphorus in the pig steel, because of the stronger reducing conditions. 2. Increased basicity of the slag does not cause the slagging of more phosphorus if the slag is very thick. 3. If a small amount of fluorspar is added to thin the basic slag, the slagging of the phosphorus is assisted. 4. Continuous operation of the furnace does not increase phosphorus in the pig steel. 5. Owing to the more oxidizing conditions in the electric furnace when pig steel is being made rather than pig iron, a greater percentage of the phosphorus is slagged.

And as to sulphur the conclusions arrived at are: 1. An increased reducing atmosphere aids in the passage of sulphur into the slag. 2. Increased basicity of the slag causes more of the sulphur to be slagged. 3. By thinning the slag a small amount of fluorspar assists in sulphur elimination from the pig steel, but an excess has the contrary effect. 4. Continuous operation of the furnace does not cause increased sulphur in the pig steel. 5. With a fluid basic slag, sulphur can be slagged readily in the electric furnace production of pig steel in both a continuous and an intermittent operation.

With steady operation in a large furnace, the loss of iron in the slag should not exceed 4 per cent of the total iron charged, depending on the amount of carbon desired in the product, but if a pig steel containing less than 0.25 per cent carbon is produced there will probably be a greater loss of iron in the slag.

An experiment was made, extending over several hours, to note the effect upon the pig steel of continuous charging and tapping rather than intermittent operation of the furnace. In addition to hematite, limestone and coke a small quantity of fluorspar was charged. A tapping was made about the middle of the run, which resulted in the following products: Pig steel, carbon 0.39, manganese 0.08, silicon 0.12, phosphorus 0.031, sulphur 0.048 per cent; slag, SiO_2 30.48, CaO 31.30, MgO 13.39, FeO 15.20, Al_2O_3 9.28 per cent.

The power consumption was 3.940 kw-hr. per gross ton of pig steel. From the product it may be seen that as good a grade of pig steel can be produced in an electric furnace when operated continuously as when operated intermittently.

The results of electric-furnace pig-iron manufacture in Sweden also show the feasibility of pig-steel production in the electric shaft furnace, as regards carbon and impurities in the pig steel and loss of iron in the slag. J. Crawford remarks as a result of his experience at Ilverhult with an electric shaft furnace: "The matter of too little carbon gives less trouble, and if the furnace is producing low silicon and carbon iron should

give none at all." From his results it appears that it is easier to operate the shaft furnace when making pig steel than when making pig iron. From the results available it seems that there should be no greater difficulty in the elimination of impurities from pig steel in a continuous shaft furnace than in intermittent operation.

In any place where there is a market for steel, and pig iron can be made at a profit in the electric furnace, it will be more profitable in the end to make pig steel for subsequent refining in an electric furnace or open-hearth, than to produce electric-furnace pig iron with a subsequent refining to steel. This is true because the power consumption has been found to be lower per ton of pig steel than per ton of pig iron, and because the time necessary for refining is reduced, which results in a greater output at a lower cost.

The results of the early experiments at Domnarfvet show that the power consumption per ton of metal produced decreased as the amount of carbon charged per ton of iron was reduced. In the latest report of the engineers at Trollhättan, it is stated that the power consumption per ton of pig iron varies in proportion to the iron content of the ore. A poor ore and pig iron high in silicon and manganese require more power than a rich ore and pig iron low in silicon and manganese. This was also found to be the case in California. The results of the writer, of course, show a high power consumption because of the small size of the furnace.

Among other expenses of pig-steel production, maintenance and capital charges would be about the same as for electric-furnace pig-iron production. The labor cost per ton of product would be a little lower for pig steel. The electrode consumption per gross ton of pig iron has been reduced to 6.7 lbs. It might be a little higher in making pig steel, because of there being less carbon in the charge, but it should not exceed 15 lbs. per ton of pig steel.

The use of pig steel in the open-hearth was tried out at Degerfors, Sweden. It was found that pig steel produced by the electric shaft furnace was more suitable for steel making in the open-hearth than ordinary pig iron, and required less time for complete refining. Normal pig iron made in the electric furnace was found to be less suited to the production of open-hearth steel than normal blast-furnace pig iron. This shows the advantage of production of pig steel rather than pig iron in the electric furnace when steel is to be the final product.

1. In the electric-furnace production of pig steel from ore, carbon in the product can be kept below 2.2 per cent, and regulated to an extent by the amount of carbon charged, without resulting in excessive loss of iron in the slag or in the production of a pig steel very high in impurities, if a fair grade of ore is used.

2. It is not difficult to slag the greater part of the silicon, phosphorus and sulphur of the charge, if the furnace is hot and the slag fluid, but conditions are less

favorable to the slagging of sulphur than of other impurities in the operation of an electric furnace for pig-steel production, which is, of course, contrary to experience in the manufacture of pig iron.

3. The loss of iron in the slag should not be excessive unless the pig steel produced is of very low carbon content.

4. From the results with the Domnarfvet, Trollhättan, and Heroult furnaces, there does not appear to be a great difficulty attending the production of pig steel in an electric shaft furnace, and in fact experience has shown that there is less difficulty in the operation of the electric furnace on pig steel than on pig iron.

5. At any place where there is a market demand for steel, and pig iron can be made in the electric furnace at a profit, the steel ultimately produced would be cheaper, if made by the electric reduction of iron ore to pig steel, followed by refining in another furnace if necessary, than if the product of the electric-reduction furnace was pig iron to be subsequently converted to steel in another furnace.

BRIQUET PRODUCTION VALUED AT MORE THAN MILLION DOLLARS.

Coal briquets to the amount of 181,859 short tons, valued at the plants at \$1,007,327, were manufactured in 1913, according to Edward W. Parker, of the United States Geological Survey. The figures for 1913 show a decrease of 17 per cent in the tonnage of briquets manufactured, but an increase of over 5½ per cent in value over the figures for 1912. Seventeen briquetting plants were in operation during the year, eight in the Eastern states, five in the Central states and four on the Pacific coast. Seven of these plants used anthracite culm or "fines," five used bituminous or semi-bituminous coal, two used carbon residue from oil-gas works, and the others used mixed coals. Coal-tar pitch is the principal binder employed, eight plants using it. Patented binders were used at five plants.

If the future of this infant relative of the coal mining industry is to be judged by the record of 1913, the judgment should be based on the increase in value rather than on the decrease in plants and in tonnage. Briquetted fuel in the United States is essentially a domestic fuel, for which there was a slackened demand in 1913, owing to the exceptional mildness of the winter of 1912-13, and of last November and December. In consequence the consumption of briquets for domestic purposes, like that of raw fuel, was generally less throughout the United States in 1913 than in either 1911 or 1912. An exception to this decrease is to be noted on the Pacific coast, where the number of operating plants increased from three to four, and the production in 1913 was exactly double that of 1912, with a gain in value of somewhat larger proportion.

Mr. Parker believes that the briquet as a domestic fuel is bound to increase in popular demand as its good qualities come into more general notice. The briquets which appear to meet with greatest favor in the Eastern States are of the boulet type, egg or pillow shaped and about the size of anthracite nut. The briquets that are practically smokeless, as they should be, make an ideal fuel for the open grate or kitchen range, holding their shape until entirely consumed and then falling, when stirred, into a pulverulent, clinkerless ash. In the Central and Pacific coast states the popular type of briquetted fuel appears to be the larger size, about that of egg coal, for which the raw materials available seem to be best adapted.

SUGAR CROP OF AUSTRIA-HUNGARY.

Complete figures for the production of sugar in Austria-Hungary during the 1912-13 season are now available. The yield of beets in Bohemia, as in all European countries except Russia, was one of the largest on record. The area cultivated in Austria-Hungary showed an advance over the preceding season of 108,680 acres, equal to 10.86 per cent. The increase in cultivation credited to Hungary was due to the location there of new sugar factories within the last two years. The number of factories in operation during the 1912-13 campaign was 201, against 196 in the preceding crop year.

Comparative data as to acreage, yield of beets, and sugar production in Austria-Hungary for the last three campaign years are given in the following table (the quantities being given in tons of 2,000 lbs.):

		Moravia, etc. ¹	Hungary and Bosnia.	Total, Austria- Hungary.
Area cultivated:				
1910-11	acres	345,500	286,500	281,950
1911-12	acres	345,800	303,810	350,740
1912-13	acres	368,030	326,040	414,960
Production of beets:				
1910-11	tons	4,985,640	3,458,510	2,833,600
1911-12	tons	2,407,790	2,909,500	3,356,870
1912-13	tons	5,400,120	3,951,200	4,652,560
Yield of beets per acre:				
1910-11	tons	14.43	12.07	10.05
1911-12	tons	6.95	9.58	9.58
1912-13	tons	14.69	12.15	11.18
Sugar content:				
1910-11	..per cent	15.80	14.50	13.60
1911-12	..per cent	14.70	15.00	14.00
1912-13	..per cent	15.90	14.60	14.00
Sugar production:				
1910-11	tons	788,370	501,380	385,330
1911-12	tons	354,090	436,700	469,370
1912-13	tons	859,870	578,930	652,960
Yield of sugar per acre:				
1910-11	tons	2.28	1.75	1.36
1911-12	tons	1.02	1.44	1.22
1912-13	tons	2.34	1.78	1.57

¹Includes Moravia, Silesia, Lower Austria, Galicia, and Bukowina.

The quality of the beets was not so good as the average, owing to long-continued wet weather in the fall. The prices paid to farmers for sugar beets of the 1912-13 crop ranged from 22.1 to 23.9 cts. per 100 lbs.



METHODS OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR INSTITUTE OF TECHNOLOGY.

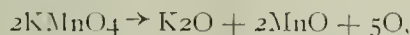
Permanganate Solutions.

Oxidation by standard potassium permanganate solution is employed as the primary reaction in the volumetric determination of a number of substances. Of these the more important are:

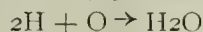
- Iron.
- Oxalic acid.
- Calcium (from calcium oxalate).
- Manganese.
- Phosphorus (in iron ore and in iron and steel).
- Hydrogen peroxide, and other peroxides.

Potassium permanganate acts as an oxidizing agent according to two distinct reactions. The one takes place in acid solutions, the other in neutral or alkaline solutions. In so much as the majority of permanganate processes are carried out in acid solutions, the reaction under these conditions is usually taken as the primary one and in making up, for example, a tenth normal solution of this salt, its reaction in acid solution is used as a basis.

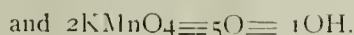
In acid solution,



when a reducing agent is present to take up the oxygen. Of course the K_2O and the 2MnO go at once to the potassium and of the manganous salts of the acid present, which is usually sulphuric acid, 2KMnO_4 is thus equivalent to ($\equiv$) 5O which according to



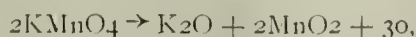
is equivalent to 10H ,



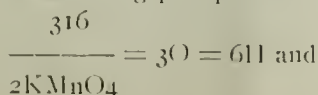
Since a normal solution is a solution which contains, per liter, the weight of active constituent which will react with one gram of hydrogen, and 316 gms. of KMnO_4 is equivalent to 10 gms. of hydrogen, it follows that a normal solution of this as an oxidizing agent salt will contain 31.6 gms. per liter, and a tenth normal solution (which is the strength usually employed) will contain 3.16 gms. per liter.

So, $\text{N}/10\text{KMnO}_4 = 3.16$ gms. per liter $= 0.00316$ gms. per c.c. for use in acid solutions.

In neutral or alkaline solutions,



the K_2O of course uniting with water to form KOH and the MnO_2 being precipitated. From this,



$\text{N}/10\text{KMnO}_4$ for use in neutral or alkaline solutions

will contain $\frac{316}{60} = 5.266$ gms. per liter.

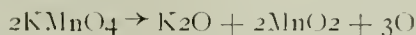
A solution of this strength is seldom used, and the term " $\text{N}/10$ per manganate" implies the solution which is tenth normal with respect to its reaction in the presence of acid.

PREPARATION OF A PERMANGANATE SOLUTION.

Potassium permanganate may not be weighed accurately and the weighed sample dissolved in the exact volume of water required because:

(1) The salt is difficult to obtain in a state of high purity. When a solution is prepared in this manner the material must be practically 100 per cent pure.

(2) All ordinary distilled water contains small quantities of organic matter which is oxidizable by permanganate with the concomitant precipitation of MnO_2 according to



the 3O reacting with the organic matter. This of course weakens the solution. This second reason, without considering the first, is sufficient to make it impossible to prepare a constant standard solution by direct weighing.

The small quantity of MnO_2 precipitated in the process of oxidizing organic matter in the water seems to catalyze the decomposition of permanganate with further precipitation of MnO_2 and the liberation of oxygen. This makes it imperative that the MnO_2 precipitated by organic matter be removed by filtration. The reduction of permanganate by organic matter or by catalysis is hastened by light. It is therefore advisable to preserve a standard permanganate solution in a brown glass bottle or one painted black.

About 3.1 gms. of pure permanganate crystals for each liter of solution desired is weighed out roughly and dissolved in the proper amount of water. The solution, in an ordinary bottle is thoroughly mixed and allowed to stand for from ten days to two weeks in order that all the organic material may be oxidized. The solution is then filtered into the dark bottle in which it is to be stored. An asbestos filter should be used. Paper is not permissible, as it introduces organic matter. It is difficult to prepare a filter of glass wool which will hold all of the finely divided precipitate. A convenient method is the following: The dark bottle is fitted with a two-holed rubber stopper, one hole carrying a six inch funnel and the other a glass tube to which exhaust may be applied. The funnel is fitted with a one to one-and-a-half inch porcelain filter plate covered with a well washed felt of

asbestos fiber. By the aid of suction, the solution filters rapidly and cleanly.

This filtered solution should be permanent enough to preserve its standard, for ordinary analytical work, for about a year. It is safer, however, to check the standard at the end of the first month, and about every three months thereafter.

STANDARDIZATION OF THE SOLUTION.

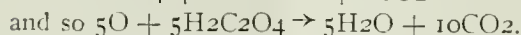
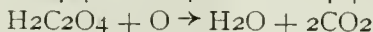
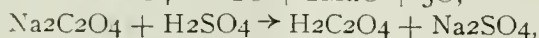
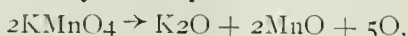
For standardizing a solution of about tenth normal strength, a number of methods are available. Of these the following are recommended:

- (1) Standardization against sodium oxalate.
- (2) Standardization against standard iron wire in the presence of sulphuric acid.
- (3) Standardization against iron wire in the presence of hydrochloric acid, for the determination of iron in iron ores.

STANDARDIZATION BY MEANS OF SODIUM OXALATE.

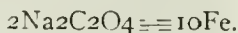
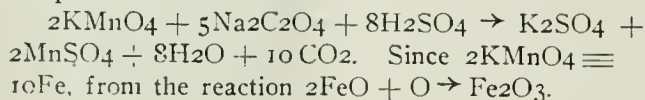
Sodium oxalate may now be obtained at little cost from the U. S. Bureau of Standards at Washington, and this material is of course, the best available for standardizing permanganate solutions. The writer has found, however, that at least one brand of sodium oxalate furnished by an American manufacturer of "Analyzed Reagents," gives results practically identical with those obtained when the Bureau of Standards sample was employed. It is, indeed, easy to prepare sodium oxalate of a high degree of purity, for the salt is beautifully crystalline and carries no water of crystallization.

The chemistry of the process is as follows:



From these expressions it is seen that

$2\text{KMnO}_4 \equiv 5\text{O} \equiv 5\text{H}_2\text{C}_2\text{O}_4 \equiv 5\text{Na}_2\text{C}_2\text{O}_4$, and the complete reaction is



Samples of sodium oxalate of 0.2000 gm. each are weighed and placed in 400 c.c. beakers. 200 c.c. of water is added, and the equivalent of about 2 c.c. of concentrated sulphuric acid, and the whole heated to about 70° C. The hot solution is then titrated with permanganate to the first pink color that lasts about a minute. The reaction between permanganate and oxalic acid is slow in starting, but rapid afterward. Care should be taken that the titration be so slow that the solution is not colored throughout by an excess of permanganate until the end.

Since $\frac{316}{2\text{KMnO}_4} \equiv \frac{559}{10\text{Fe}} \equiv \frac{670}{5\text{Na}_2\text{C}_2\text{O}_4}$
and 0.2 gm. samples of oxalate are used,

$$316 : 670 :: X : 0.2$$

$$0.2 \times 316$$

$$X = \frac{670}{0.2 \times 316} = 0.0943 \text{ gm. KMnO}_4$$

$$\text{and } 559 : 670 :: X : 0.2$$

$$0.2 \times 559$$

$$X = \frac{670}{0.2 \times 559} = 0.16565 \text{ gm. Fe.}$$

$$0.0943$$

$$\text{Then } \frac{0.0943}{\text{No. of c.c. used}} = \text{weight KMnO}_4 \text{ per c.c.}$$

$$0.16565$$

$$\text{and } \frac{0.16565}{\text{No. of c.c. used}} = \text{standard in terms of iron.}$$

$$\parallel$$

Since $1 \text{ Fe} \equiv 1\text{H}$, and $\text{N}/10 \text{ Fe}$ solution contains 5.59 gms. per liter or 0.00559 gm. per c.c.,

$$0.00559$$

then $\frac{0.00559}{\text{Fe standard}} = \text{factor of N}/10 \text{ of the perman-}$
ganate solution.

STANDARDIZATION BY MEANS OF IRON WIRE IN SULPHATE SOLUTION.

Standard iron wire, as furnished by chemical supply houses, with the percentage of iron given (usually about 99.8% Fe) gives results, when properly treated, which are practically identical with those obtained by the use of sodium oxalate.

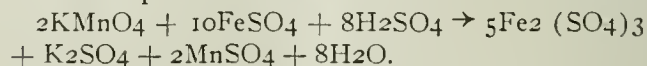
Samples of 0.2000 gm. are weighed out and the weights multiplied by the factor for iron, giving the true weight of iron. 50 c.c. of 20% sulphuric acid is placed in a 250 c.c. Erlenmeyer flask, which is fitted with a rubber stopper carrying a Bunsen valve. Into the acid is dropped from one to two grams of sodium bicarbonate in order that the air may be replaced by carbon dioxide, and then the sample of wire is introduced and the flask stoppered by the Bunsen valve. The whole is then boiled gently until the iron is completely dissolved, and the boiling continued for a minute or two more. The solution is now cooled, and, after dilution to 150 c.c., titrated to the first permanent pink.

Net weight of iron

$$\frac{\text{Net weight of iron}}{\text{c.c. used}} = \text{iron standard.}$$

The atmosphere of CO₂ and the Bunsen valve are employed so that oxygen may be kept out of contact with the hot solution. Under these conditions the iron goes into solution completely as FeSO₄. The boiling after complete solution is necessary in order that all traces of hydrocarbons from the carbon present in the iron may be expelled. Hydrocarbons reduce permanganate.

The complete reaction is:



STANDARDIZATION BY IRON IN THE PRESENCE OF HYDROCHLORIC ACID.

In the determination of iron in iron ore, it is general practice, on account of the great convenience and

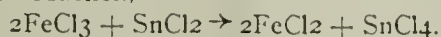
speed of the method, to decompose the ore with hydrochloric acid in the presence of an excess of stannous chloride, remove the latter by oxidation, reduce the ferric chloride again with stannous chloride, using the least possible excess, remove this excess of reducing agent by the addition of mercuric chloride, and titrate the ferrous chloride with permanganate in the presence of an excess of the so-called "preventive" or "guard" solution.

There is a fundamental error involved in the titration of iron in the presence of hydrochloric acid on account of the direct oxidizing action of permanganate upon hydrochloric acid with its accompanying reduction of the permanganate, resulting in the use of more permanganate than is demanded by the iron alone. This error may be almost entirely overcome by keeping the concentration of hydrochloric acid low, and titrating in dilute solution in the presence of from 30 to 40 c.c. of a strong solution of MnSO_4 , H_2SO_4 and H_3PO_4 ; the "guard" or "preventive" solution. The action of this manganous solution has been explained in several different ways, and is being further studied by several investigators. No explanation is given here, the fact being sufficient for present purposes.

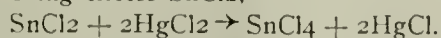
There is sufficient probability of constant error in the titration in the presence of HCl to make it advisable to standardize by a process parallel to that used in the determination.

Samples of standard iron wire of 0.2 gm. each are placed in Erlenmeyer flasks (250 c.c.) and dissolved by boiling with 10 c.c. of 1:1 HCl . When the wire is completely dissolved (the solution being yellow), the flask is removed from the source of heat, and to it is added drop by drop, from a pipette, a 5% solution of stannous* chloride. About 5 drops should suffice to decolorize the solution, indicating complete reduction to the ferrous state. The stannous chloride should be added slowly and any unnecessary excess avoided. While the reduced solution is cooling, about 200 c.c. of water and 25 c.c. of a saturated solution of mercuric chloride are placed in a 500 c.c. beaker, and into it is rinsed the reduced solution from the flask. A white, silky precipitate of mercurous chloride is produced, all of the excess SnCl_2 being changed to SnCl_4 . This precipitate should be small in amount, as much of it masks the end point in titration, and causes error. After standing a few minutes, 30 c.c. of "preventive solution"† is added and the whole made up to 400 c.c. and titrated slowly with permanganate. The pink color at the end should last about a half minute.

In the reduction,

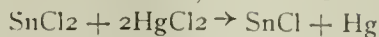


In removing excess SnCl_2 ,



The reduced solution is poured into the mercuric chloride so that there may be present at all times an

excess of the latter reagent. If, for only an instant, the SnCl_2 were in excess, the reaction



would take place. This is indicated by a gray or black precipitate of metallic mercury, instead of the pure white of the HgCl . If this should occur, the determination must be discarded.

The standard obtained as above will differ slightly from that given by the titration of iron in the presence of sulphuric acid, or from sodium oxalate. It should therefore only be employed when the corresponding method is to be used in the analysis.

PRODUCTION OF HYDROGEN FROM WATER UNDER HIGH PRESSURE.*

Progress of chemical knowledge often comes from the progress of experimental possibilities and improvement of experimental methods. Thus high temperature chemistry grew from the introduction of electrical methods into the chemical laboratory by which chemists were enabled easily to produce high temperatures. At the same time the electrical and optical methods of measuring these temperatures were so much refined that the handling of such experiments ceased to be difficult. Laboratory results were soon made use of in technical work and now we have large industries based upon methods of electrical heating.

One very recent method introduced into the laboratory is that of handling very high pressure conveniently and without danger.

Chemical reactions under pressures higher than that of the atmosphere are not unknown in the laboratory and in chemical industry, but they have been characterized by their purely qualitative nature and the limited height to which the pressure could be raised. The former was due to the lack of appreciation of the extent to which chemical reaction may be influenced by pressure, and this in general led to a mere attempt at raising the temperature of a liquid component of a chemical reaction above its boiling point. The second restriction lay in the inadequacy of technique and in the construction of the retaining vessels.

Modern physical chemistry teaches us that besides this application of pressure so often employed there are other ways of influencing chemical reactions by means of pressure. For instance, the law of mass action tells us when and in what direction an equilibrium will be changed by an increase of concentration, that is of pressure of any one component of a chemical reaction.

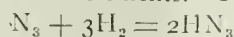
Monogeneous gaseous reactions under the influence of pressure are forced in the direction in which a reduction of the number of molecules takes place. A chemical reaction can therefore be carried further by an increase of pressure whenever the reaction is accompanied by a diminution of volume.

*From "Journal Society of Chemical Industry."

*50 gms. stannous chloride crystals, 100 cc. conc. HCl , made up to a liter with water and kept reduced by means of some pieces of metallic tin.

†70 gms. $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$, 600 cc. water, 130 cc. conc. H_2SO_4 and 140 cc. H_3PO_4 sp. gr. 1.7.

An excellent example of this sort is the synthesis of ammonia from its elements. The equation



shows that four molecules of the mixture of nitrogen and hydrogen give two molecules of ammonia, giving a diminution of molecules or a decrease of volume. The formation of ammonia must therefore be carried further by increased pressure. The utilization of this fact made possible the technical synthesising of ammonia. This reaction is carried on at about 200 atmospheres, and at temperatures between 500° and 600° C.

When a gas enters into reaction with a liquid or a solid to form a new liquid or solid substance, it is evident that pressure must further chemical combination as predicted by the law of Le Chatelier. Heterogeneous reactions under very high pressure have not yet been used on a large scale, but according to my own results it is possible to effect, for instance, the oxidation of calcium oxide to peroxide by means of gaseous oxygen. At atmospheric pressure no appreciable reaction takes place, not because reaction cannot take place, but because the speed of reaction is too slow. Reaction velocities increase with higher temperatures, but the dissociation increases also, and under pressures above 100 atmospheres it was possible to cause formation of the peroxide from ordinary limestone.

Other examples of similar reactions are in the extensive researches of Ipatiew on the hydrogenation of various organic compounds in the presence of catalysts at high pressures. He was able, for example, to obtain alcohols from ketones and succeeded in displacing some metals from aqueous solutions of their salts by hydrogen under pressure. Thus copper, silver and mercury were precipitated from solutions of their sulphates under 100 atmospheres with formation of sulphuric acid.

A third possibility of the application of high pressure for promotion of chemical reaction lies in the ability to retain the liquid state from the boiling point up to the critical point. The physical properties of a liquid may therefore be utilized at high temperatures, making reactions possible which at low temperatures cannot be carried out. Furthermore, the physical properties of a liquid may undergo remarkable changes between the boiling point and the critical point, as for instance the electrolytic dissociation of water. According to A. A. Noyes the dissociation of water increases between these temperatures nearly 2,000 fold.

This suggests that water must act as a fairly strong acid or base at high temperatures, provided it is kept in the liquid state. In the presence of a metal we may expect therefore a reaction with evolution of gaseous hydrogen. Led by this assumption, I have undertaken in collaboration with my assistant, Herr Specht, a series of experiments on the action of liquid water in metals, particularly on iron, and we believe to have found in this reaction a basis for a new technical process of generating hydrogen.

Since iron and water are the sole reacting substances, it is evident that it is impossible to obtain an extremely pure gas, mainly because the impurities of iron are practically not attacked by the acid water. The gas has been analyzed and shows:

	Per cent.
Hydrogen	99.9495
Carbon monoxide.....	0.0011
Saturated hydrocarbons.....	0.0416
Unsaturated hydrocarbons.....	0.0078

The speed of reaction naturally depends on the temperature, but it is also affected by the presence of electrolytes such as sodium chloride or ferrous chloride. The presence of a noble metal also accelerates the attack of the iron.

This is shown by the following table:

	Temp.	Quantity of Hydrogen per Hour.
Iron and pure water.....	300°	230
" " " " Fe Cl ₂	300°	1,390
" " " " Fe Cl ₂ + Cu.....	300°	1,930
" " " " Fe Cl ₂ + Cu.....	340°	3,450

Within the limits practically obtainable, the speed of reaction is so great that in a retaining vessel of 10 gallons capacity about 3,000 cubic feet a day may be generated. A great advantage of this method lies in the fact that the hydrogen is at once under high pressure and may be filled into cylinders without compression. It is evident that between the generator and the steel bottle in which the hydrogen is collected a reflux condenser must be used in order to condense the water.

It is, furthermore, of the highest importance that the oxidation does not take place merely on the surface but penetrates the iron and oxidizes it quantitatively to Fe₂O₄, according to the equation—



The latter is precipitated as a finely divided powder readily reducible by carbon or carbon monoxide, and can therefore be regenerated and re-enter the cycle process. This reduced the total expense of the process to that of the reduction of Fe₃O₄ and the energy required for heating the reacting mass with mainly liquid water to about 300°.

Compared with the latest and cheapest technical process, that of Linde-Frank-Caro, which separates hydrogen from carbon monoxide by liquefaction of carbon monoxide and other impurities of water gas, this new method offers the advantage of producing a very much purer gas without cost of purification, without cost of impression, and without any movable parts in the apparatus. The total energy expended is derived from coal, using only about 60 per cent as compared to the Linde process, and the apparatus is not only much cheaper, but requires less space for the same output. The first experimental plant in Hanover has a capacity of about 1,000 cubic feet an hour, generated in 6 high pressure vessels of about 10 gallons each.

AMERICAN RADIUM MINES AND RADIUM RESEARCH LABORATORY.

By FRANK G. PERKINS.

The accompanying illustrations, Figs. 1 and 2, show the equipment of an American Research Laboratory, which is doing important work in connection with the ore from the radium mines in Colorado. These ore lands are located in Paradox Valley, Montrose County, Colorado, and the ore is known as carnotite, which consists of uranium, vanadium and radium.



Fig. 1. Main Laboratory.

A chemical concern of Pittsburgh, Pa., acquired 91 claims, covering an area of about 1,000 acres, and has been working the mines for some time. So far the monthly output of ore has been about 100 tons, which has yielded a gram of radium. A gram, of course, is not a large quantity, but when it is considered that there is only about one ounce of radium in existence, and that a gram is worth about \$120,000, it is not difficult to realize the value of this metal.

The ore lands are located in the foothills of the Uncompahgre mountains. The ore is recovered in bags, which are packed and shipped on the backs of burros through the hills for a distance of 20 miles. Here they are loaded on wagons and hauled to Placerville, which is the nearest railroad station. The ore is then shipped by rail to Cannonsburg, Pa., where the ore reduction mills are located. In these mills the product is reduced and the radium values are extracted, which upon their recovery are taken to the radium research laboratories shown in Figs. 1 and 2, in the city of Pittsburgh, where the final process of refining the radium values is carried on. The radium values are here produced by a refining process until all its component parts are segregated. This work is exceedingly delicate and requires machinery of the most delicate character. To obtain an idea of the minuteness of this operation it may be stated that one part of radium in 10,000,000,000 of other matter is easily determined. Not only the radium raw chlorides are refined and the pure radium is recovered from them, but the analyses for the mines and the mills are done here, and important researches on methods for chemical treatment and for the application of radium are carried on.

The radium research laboratories are in charge of Dr. Otte Brill of Vienna, Austria, formerly assistant to Sir William Ramsey of London, England, himself one of the foremost authorities of radium research. Dr. Brill has introduced into the laboratory many improvements, so that the processes and methods used here are said to be much quicker and also more accurate than the older ones.

It may be stated that in the refining department the radium values go through a complete chemical process. The chlorides pass from retort to dish again and again until they are purified so as to contain from 10 per cent to 100 per cent radium chlorides. The eye of the expert can quickly follow the rate of purification from the color of the salt. While the raw chlorides are in appearance not much different from common table salt, the radium chloride, as it gets more concentrated, acquires more and more a yellowish and brown tint, at the same time the glass and porcelain dishes in which the high power salts are kept are getting more and more purple colored from the rays of the radium.

Although this is only a rough way of estimating the strength of the radium preparation, the real analysis is carried on in the physical department of the laboratories. The methods applied here for the purpose of analysis are not only exceedingly delicate, but also peculiarly interesting. These analyses are not of the ordinary chemical nature, but they are physical methods, the electrical properties of the radium being used for the determination of this substance. It is well known that each particle of radium gives out or projects electric rays, which makes the air a conductor of electricity. This conductivity of the air produced by the rays of radium is measured by a sensitive electrometer of especial construction, and by this means a most accurate measure of the amount of radium in the prep-



Fig. 2. Measuring Particles of Radium.

aration is obtained. The physical department, beside making the control analysis for the process in the mill and the refining department carries out also a considerable number of radium determinations in ores, which are brought to the laboratory to be tested for radio-activity.

METALLURGY

LEACHING OF COPPER TAILINGS.*

By RUDOLF GAHL, PH. D.

The electrometallurgy of copper is mainly hydrometallurgy, inasmuch as the electric current is used principally for the deposition of copper from its solutions. Up to the present time the application of the current has been confined to the precipitation of copper from solutions originating from metallic copper, in other words to the electrolytic refining of copper, but the application of electricity to copper solutions resulting from ores is being constantly advocated, and as a matter of fact is being tried in several places on a small scale. The necessary basis for electrolytic precipitation of copper extracted in leaching operations is naturally a successful application of leaching methods, and from this standpoint a presentation of experimental results in this line may be justified for an electrochemical meeting, although the electric current was not used in these tests for the precipitation of copper.

The leaching of carbonate ores of copper has been attempted repeatedly, but has not been a commercial success, except in some isolated cases, as for instance in the case of the Arizona Copper Co. at Clifton, where such leaching operations have been carried on for a great number of years. The frequent failure of such attempts may have been the cause for the general distrust of leaching operations that prevailed among engineers up to a few years ago. Recently this sentiment has changed considerably and leaching plants of large size are being planned. I might mention in this connection the projected Chuquicamata plant in Chile and the Ajo project of the Calumet and Arizona, where it is intended to leach oxidized ores by sulphuric acid.

Engineers are even no longer afraid of giving their attention to the hydrometallurgical treatment of sulphide ores, as for instance the porphyry copper ores. Since the milling of these ores has been undertaken on the present enormous scale, the gravity concentration process by which they are treated has been the subject of extensive study at the plants. And while this research work has shown ways for essential improvements which, for instance, make the concentration of ores possible that nobody would have thought of milling some years ago, it has, on the other hand, clearly defined its limitations.

The concentration process has been developed to such a state of perfection that on clean sulphide ores

recoveries of 85 per cent of the copper can be obtained. Unfortunately the ores that generally are called porphyry copper ores are not of this character, as they contain a considerable percentage of their copper in the oxidized state. This is undoubtedly partly due to the fact that the limits between sulphide and oxidized ores are not very sharp or are not followed exactly when the ore is mined. On the other hand most of the ore bodies that are mined at present are to some extent altered by oxidation.

The water concentration process is, up to the present time, not able to extract copper in oxide combination with an efficiency, approximating the extraction of the sulphide copper. I believe that 30 per cent is an average round figure for the extraction effected on the oxidized portion of the copper in sulphide ores. It follows that where ores are largely contaminated with such material no satisfactory saving can be obtained by ordinary concentration methods. A great many of the mines in Arizona and New Mexico suffer under this disadvantage (Chino, Shannon, etc.).

The natural consequence has been that the copper mines have been looking lately towards a hydrometallurgical method to improve the copper extraction. Just where the hydrometallurgical method would come in has been a point of much discussion among copper metallurgists. In fact they are divided into two factions in regard to this question.

The one party, which we might term the radical party, is advocating attempts to discard the time-honored concentration method and to supplant it by an altogether different treatment. They suggest to roast the ore, to leach the calcines and to precipitate the copper from the resulting solution. Electrolytic precipitation is favored by many, although it is maintained by others that the precipitation of copper from so low-grade solutions as would naturally result from leaching very low-grade ores is a problem which so far has not been solved by electrochemistry.

Among the men who propose such processes I might mention Keith, Laszczynski, Greenawalt, Smith, Wedge, McKay, Robertson, Slater, Van Arsdale, Antisell, David, Pope, and Hahn. Although replacing the concentration process by a process of the kind indicated at one of the prominent Western mines would mean a radical departure, it must be kept in mind that similar processes have been in constant use for a long time both in Europe and in the East of the United States. The Pennsylvania Salt Mfg. Co. has produced copper in such a way for years.

The class of copper metallurgists which we may call the conservative party have confined themselves

*Paper presented at the 25th General Meeting of the American Electrochemical Society, in New York City, April 16-18, 1914.

to supplementing the concentration process by hydro-metallurgical methods. This can be done by leaching the concentrates, which I understand is being tried at the Braden Copper Co., and by leaching the tailings. The latter is the more important, inasmuch as it adds to the extraction effected by the concentrator. To this class belongs the system of leaching worked out by Laist at the Anaconda, the tests with the Bradley process also at Anaconda, and tests undertaken at some of the Arizona mines.

It has been my task for a number of years to study the losses connected with the concentration of ores and to suggest remedies. I became convinced at an early stage that for many ores supplementing the concentration by leaching would be the only possible remedy, and, for this reason, I have made extensive experiments along the lines which I designated as conservative above. I will try to outline one of these experiments in the following:

The test was made at Morenci, Arizona, in connection with the concentrating plant of the Detroit Copper Co. The ore has the characteristics of the porphyry copper ores, being perhaps oxidized and kaolinized to a higher degree than other ores of the class. The principal copper mineral is chalcocite. Some chalcopyrite and some pyrite accompanies it. In concentrating, ores of this character behave in a typical way. The resulting sand tailings are always low in copper or can be reduced to a very low figure by ordinary milling methods, that is, regrinding and re-concentration. The slime tailings, however, are high in copper contents, and no standard method of milling is available to reduce them materially. The existence of so much copper in them was in this case and in many other cases due to the accumulation of oxidized material in the slime. The oxidized portion of the ore has evidently a greater tendency to form slime than the sulphide portion, and as the recovery in oxide copper is very low, it is a common thing to find more oxide than sulphide copper in the slime tailings.

It was attempted in the experiments to be described to recover the oxide copper in an economical way by leaching with dilute sulphuric acid.

This may seem easy, and, as a matter of fact, it proved not to be extraordinarily difficult, but nevertheless was considered hopeless in the beginning by men of great experience in the metallurgy of copper. It is due to the confidence which Mr. C. E. Mills (at that time general superintendent of the Detroit, now general manager of the Inspiration Consolidated Copper Co.) had in the outcome, that a suitable testing plant was built in which this experiment could be made.

Successful leaching not only depends on getting the copper into solution; it depends just as well on the separation of liquids from solids and on the precipitation of copper from the resulting solutions.

In this case the second step seemed especially difficult, and the slime in question is very colloidal in char-

acter and behaves almost like clay. Filtering costs with this slime would probably have been prohibitive, not even considering the extra costs which the acidity of the solution would have imposed.

For this reason I looked towards a decantation method which would suit this particular purpose. Such method, in addition to eliminating the difficulty in question, would also offer the following advantage over filtering. Where filtering is adopted in large-scale leaching operations, that is, especially in the treatment of gold and silver ores in connection with the cyanide process, the pulp is agitated with cyanide solution until a sufficient dissolution of the metal values has taken place, then it is sent to the filter presses or vacuum filters, as the case may be.

It was found in preliminary copper leaching experiments that it is far more economical to leach in steps, that is, to leach fresh ore first with a solution high in copper and low in free acid, to replace this solution by another one lower in copper and higher in acid, to finish the leaching with a solution still lower in copper and higher in free acid. This reduces the consumption of chemicals and raises the extraction. It has also another advantage when the precipitation of the copper is affected by iron, as was the case in these experiments. By bringing nearly exhausted solution in contact with fresh ore, as described, the ferric salts are transformed into ferrous salts, and the consumption of metallic iron is reduced nearly to the theoretical limit. The loss of iron resulting from the entrance of ferric salts into the precipitating plant is thereby very materially reduced. Filtering methods do not lend themselves to a repeated change of solutions.

Continuous decantation has, it seems, been originated by John Randall of Deadwood, S. D. He evidently clearly recognized the importance of finishing the cyanide treatment of an ore with fresh solution, and developed what is called now the counter-current system of leaching. Mr. J. V. N. Dorr of Denver has, I believe, applied this system in several cyanide plants. If I understand Mr. Dorr right he makes it a point in his installations to finish the leaching before he sends the solution to the decantation system. He, therefore, practices rather counter-current washing than counter-current leaching. Lately Mr. John Rothwell,¹ of Denver, has called attention to the in-aniding and suggested a flow-sheet based on this system.

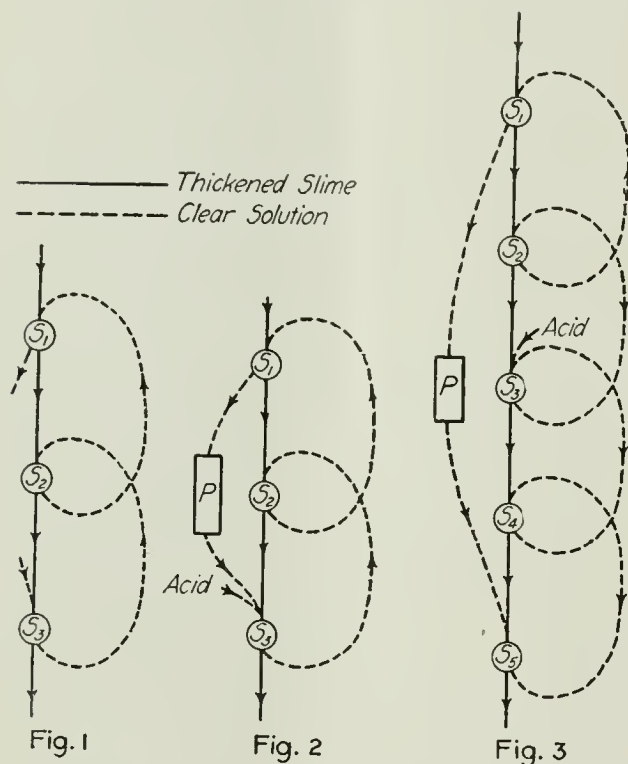
Randall's flow-sheet taken from his U. S. Patent 708,494, Sept. 2, 1902, is represented in Fig. 1 in a diagrammatic way. It shows only the settling tanks, S_1 , S_2 , S_3 , the mixing tanks, one of which in the inventor's arrangement precedes each leaching tank, being left out of consideration.

Thickened slime enters the tank S_1 , after having been mixed with solution pumped to the head of the herent advantages of counter-current leaching in cy-

¹Met. and Chem. Eng., 9, 439 (1911).

tank. It makes two products, a spigot discharge of thick slime flowing to S_2 , after being mixed with the solution pumped to the head of tank S_2 and an overflow of clear solution which is the product of the leaching operation and may be sent to a precipitating plant.

Settling tank S_2 makes also two products, thickened slime which goes to the next settling tank in the series after having been mixed with fresh solution entering the system, and a clear overflow which is pumped to the tank ahead in the series.



In the same way settling tank S_3 makes two products, thickened slime which goes to waste and a clear overflow which is pumped to S_2 , the tank ahead in the series. Only three tanks are indicated in the diagram, but the number is, of course, immaterial. It will be noticed that the solvent fluid first enters at the last tank S_3 , mixing, while fresh and strong, with the exhausted solids and then passes down through the series.

While this flow-sheet represents the characteristics of counter-current leaching, it can be improved upon for the leaching of tailings slime. The fresh acid solution (for cyanide operations the word cyanide should be substituted for acid) enters the last tank of the system, and, as a part of this acid stays with the settled pulp, this fraction of the acid is lost. There is also another drawback. The leaching power of the solution in the last tank being the highest, it is very likely that leaching may still take place in this tank. If it does, it means that some copper is lost along with the acid. For this reason a sufficient number of tanks has to be provided and great care to be exercised in the operation so that leaching does not extend to the last tank.

In the installations described in the metallurgical literature this drawback is frequently avoided by adding another tank or two to the system in which clear water is used for the purpose of washing the settled pulp that would result from the application of the flow-sheet, illustrated in Fig. 1.

In cyanide plants there is no objection to using solutions resulting from the leaching operations in the milling department, as the cyanide has no detrimental effect on milling machinery. Crushing in cyanide solution is in fact frequently preferred. For this reason it is possible to add the fresh water (which is required to make up for the water going to waste with the tailings) in the cyanide department and to send an equivalent amount of cyanide solution to the milling department. In the cyanide department the fresh water can be used for washing the tailings resulting from the leaching operations, and this is, as mentioned above, ordinary practice.

It is not possible, however, to do this, when leaching is carried out in sulphuric acid. The resulting solutions, being unfit for use in the mill, have to be retained in the leaching department. As new quantities of water enter the leaching department all the time, solutions would accumulate, if the attempt were made to use fresh water for washing. For this reason the barren solutions coming from the precipitating plant are essentially the only ones that are available for washing the settled pulp.

Keeping in mind, that no fresh water can be used in leaching copper tailings, it follows, that the leaching plant has to be independent of the mill and that no circulation of solutions must take place between the two. The flow-sheet of the leaching plant has to be essentially a closed circuit. The only thing to do then with solutions, as they would result from counter-current leaching on Randall's plan, would be to send them to a precipitating plant and from there, having added fresh acid, to the last tank. This would result in a flow-sheet as shown in Fig. 2.

This flow-sheet can be changed in such a way, that the objections raised against the system are obviated. Fig. 3 shows the resulting modifications. Two more tanks, the number, of course, is not essential, are added to the system and serve for washing purposes. The solution discharging from the precipitating plant is sent to the last tank of the series and passes through the series of tanks in counter movement to the pulp.

Comparing Fig. 3 with Fig. 2, it is evident that there is no difference in the flow-sheets except regarding the condition of the pulp at various points of the system. While in Randall's flow-sheet the fresh solution enters at the tail end of the system, the solution from the precipitating plant, low in copper and low in acid, does so in the modified system. On the way through the series of tanks, it is charged with fresh acid and continues its journey through the system. In this manner the first tanks (counting in the direction of the

flow of the thickened pulp) serve mainly as leaching, the others as wash tanks.

By the way, I might call attention to the possibility of applying heat to a system like this, although no use has been made of artificial heat in the experiments made with this plant. If heat in the form of steam or otherwise is applied at the same point or near the point, where the acid is added, as marked in Fig. 3, the temperature, after equilibrium is reached, will drop toward the tail end of the system, as will easily be seen by tracing the way in which the heat distributes itself. Accordingly only part of the heat introduced escapes with the tailings pulp, while the rest serves to preheat the inflowing pulp.

I have been emphasizing the importance of adding acid in the most suitable place of the system. To anyone who has used similar methods in cyaniding gold and silver ores, it may seem as if this point would not deserve so much consideration. But there is a radical difference between copper leaching and cyaniding in regard to this point.

In cyaniding there is always a large excess of the leaching agent over the quantity which is required to combine with the metal values contained in the ore. The cyanide solution charged with gold and silver will pass through the precipitating plant and emerge from it as a solution which is available as leaching liquor again. The loss in cyanide is so small, that it can be made up in almost any part of the circuit without causing much difference in the extraction. Conditions are different in copper leaching. The solution leaving the precipitating plant is useless for leaching purposes. This means, that sufficient acid has to be added to make it a solvent for copper minerals, and it is, of course, of utmost importance to add this acid where it will accomplish most good.

I will not describe in detail the plant which was constructed along the lines indicated in the flow-sheet. It may suffice to state, that it consisted of a series of ordinary settling and small agitating tanks of the simplest kind. The pulp was transferred by gravity, the solution was circulated by air-lift. A launder filled with scrap-iron served as a precipitating plant. The plant treated between 7 and 10 tons daily for a period of 50 days continuously. It was closed down only for very short intervals and only when owing to shut-downs of the concentrator the feed for the leaching plant gave out. One unskilled laborer per shift was sufficient to operate the plant; in fact, would be for a large plant, except when it was necessary to remove the cement copper and to add iron in the precipitating plant.

The conditions of the tests were varied, as far as quantity of acid and tonnage are concerned. No heat was applied. Under the best conditions a recovery of 60 per cent of the copper contained in the tailings slime was obtained from material containing 1.24 per cent Cu.

The 60 per cent of the copper extracted represents the copper existing in the oxidized state. A higher extraction could have been obtained by using ferric sulphate in connection with sulphuric acid. Methods for cheap production of this salt were worked out in the laboratory, but have not been tried yet on a larger scale.

The probable operating costs of a leaching plant for tailings slime were calculated on the basis of the experiments, with a certain margin for safety. They are represented in Table I. The tailings slime being ordinarily a waste-product was considered not to cost anything.

TABLE I—PROBABLE COST OF LEACHING TAILINGS SLIME PER POUND OF COPPER DELIVERED AT NEW YORK.

3.50 lbs. acid @ \$10.00 per ton H_2SO_4	1.75c.
1.50 lbs. of scrap iron @ \$19.00 per ton.....	1.43c.
Power	0.25c.
Labor and repairs.....	1.00c.
Smelting, refining, transportation of Cu, including losses in smelting, etc.....	2.00c.
Interest and depreciation of plant.....	1.00c.
Total	7.43c.

The figures are based on conditions prevailing at Morenci, Arizona, where the tests were made. Owing to the location of this mining camp freight rates are rather high.

Acid.—The acid consumption is taken at 3.5 lbs. H_2SO_4 instead of 3.16, the figure obtained in the tests. The rate of \$10 per ton of H_2SO_4 is based on the assumption, that it would be possible to obtain the acid from a near-by smelting center, where large quantities of ores high in sulphur are roasted.

Iron.—The iron consumption was assumed to be $1\frac{1}{2}$ pounds of scrap iron instead of 1.25 pounds pure iron. The price of the scrap iron is so high because it has to be hauled from Eastern Texas.

Power.—Owing to the relatively small scale on which the experiments were carried out, it was impossible to ascertain directly the power consumption for large-scale operations. It was estimated from figures about power consumption of air-lifts and agitation found in text-books, etc. Power cost was assumed to be 36 cents per H. P. day.

Labor and Repairs.—Labor for leaching was found to be, and repairs were expected to be, equally negligible for a well-constructed plant. Labor and repairs in connection with the precipitation were based on what it was thought could be accomplished in a copper precipitation plant, the operating cost figures from which were available.

Smelting, Refining, Transportation of Copper, etc.—This item is based on the assumption that the smelting of the precipitate would be done in converters and includes the losses to be expected by this treatment.

Interest and Depreciation of Plant.—This item is hard to approximate without making definite plans. The figure assumed may serve as an upper limit, however, and may be ample enough also to include taxes and a proportionate share of general office expenses.

As mentioned above only 60 per cent of the copper contained in the tailings slime was extracted by leaching with dilute sulphuric acid, as the rest of the copper existed in the form of sulphide which is not acted upon by dilute sulphuric acid. Since making these tests the flotation process has been applied to ores of similar character and it has been found that it effects a very much higher extraction on the sulphide portion, an almost negligible one on the oxide portion of the copper. It follows, that tailings from flotation plants are lower in sulphide and higher in oxide copper. The fact has also been established that the oil used in the flotation treatment of ores does not interfere with a successive leaching of the tailings (L. R. Wallace, formerly Metallurgist Inspiration Consolidated Copper Co.), it evidently does not attach itself to particles of oxidized copper minerals.

It seems that the conclusion may be drawn with safety that for certain classes of copper ores a combination of a flotation and a leaching process constitutes a metallurgical treatment which it will be difficult to surpass by other metallurgical processes in efficiency and cheapness.

I am greatly indebted to Dr. James Douglas, president of the Detroit Copper Mining Co. and of Phelps, Dodge & Co., for his permission to describe the Morenci leaching tests.

MINING AND MINERALS OF CHINA.

In a recent consular report Consul General Thomas Sammons, Shanghai, discusses mining conditions in China as follows:

Poor means of transport and communication, antiquated methods of mining, and the restrictions of the mining regulations have prevented the development of all but a small part of China's vast mineral resources. Article IX of the Mackay treaty of 1902 provided that China would recast her mining regulations in such a way as, while promoting the interests of Chinese subjects and not injuring in any way the sovereign rights of China, shall offer no impediment to the attraction of foreign capital or place foreign capitalists at a greater disadvantage than they would be under generally accepted foreign regulations. New mining regulations were promulgated in 1902 and again in 1907, but they have never been entirely acceptable to the foreign governments concerned. Press reports indicate that the regulations are again being revised by the Peking authorities.

The mineral wealth of the country consists chiefly of coal and iron, but antimony, tin, copper, and zinc are also produced in considerable quantities. So far as my own consular district is concerned, the Province of Chekiang is known to contain coal (chuchowfu), lime, gypsum, alum (pingyang), and building stone, and the Province of Kiangsu, coal, iron, marble, and plumbago. The extent of these deposits and their

value is not known, and, with the exception of building-stone quarrying, no serious endeavor has ever been made to exploit the mineral resources of these Provinces, which are probably amongst the poorest in the country.

The Provinces contributing most heavily to the present coal output, estimated at 9 million to 13 million tons a year, are Chihli, the Manchurian Provinces, Shansi, Shantung, Honan, Kiangsi, and Hunan. Of foreign concessions, the principal are those of the Peking Syndicate (Ltd.), British, operating mines at Chinghuachen, Honan (head China office, Tientsin); the Shantung Mining Co. (Schantung Bergbau Gesellschaft), German, operating in Shantung (offices at Tsingtau); and the South Manchuria Railway Co., Japanese, operating the Fushan Collieries in Manchuria (head office, Mining Department, Dairen, Manchuria).

Of joint Chinese and foreign concessions, the most important is the Kailan Mining Administration (a combination of the Chinese Engineering & Mining Co., British, and the Lanchow Mining Co.), Chinese. This administration operates very important collieries in the Kaiping Basin; head office, Tientsin.

The following joint concessions are also noted in the China Yearbook, 1913:

Mentoukou Colliery (Anglo-Chinese). Owned by the Tung Hsing Sino-Foreign Coal Mining Co. (Ltd.), and financed with Chinese and foreign capital. Development hindered by disputes as to ownership. Doney & Co., Tientsin, agents.

Chinghsing Collieries, Chihli. Owned by Sino-German company and the Chinese government. German engineers.

The following is a list, from the same source, of Chinese coal mines with foreign machinery:

Pao Chin Collieries, Pingtingchou, Shansi. Owners, the Pao Chin Mining Co. of Shansi.

To Li Mines, owned by a Chinese syndicate. On Peking-Hankow Railway.

Lin Cheng Mines, on Peking-Hankow Railway. Chinese company; Chinese co-manager and engineer, and Belgian managing engineer.

Pinghsiang Mines, Kiangsi, owned by the Hanyeh-ping Iron & Coal Co. (Hanyang Iron Works), Hankow.

Tan Shan Wan Coal Mine, Hupeh. Owned by Hupeh provincial government.

Poshan Mines, Shantung. Chinese company.

Lung Wang Tung Mines, near Chungking, Szechwan. Owned by Chiang Ho Mining Co. (Chinese).

Iron ore is found almost in every Province, but only in a few districts is it worked on an extensive scale. For a discussion of the iron and other mineral resources of China, reference might be made to a paper read by Mr. T. T. Read, late professor of metallurgy, Peiyang University, before the American Institute of Mining Engineers. The principal mines working are the:

ital engaged in operating the mines or loaned to the mining companies. China also has a number of young Chinese mining engineers educated abroad who are taking charge of work in this country. An American mining engineer has been in the Far East for some time, working in Manchuria and China and at other places, principally in inspecting mining properties.

When the Chinese mining regulations are in such form as to permit the joint development of the vast mineral resources of the country by foreign and Chinese capital, there will undoubtedly be opportunities for foreign mining engineers; to the extent that American capital is interested, for American mining engineers. There may, of course, also be some opportunity for American engineers in inspecting properties, but at present I fail to see any opening for them in China. Of course a young engineer might be able to obtain employment in one of the Government colleges as instructor in metallurgy and have an opportunity to examine into the mineral resources of the country and make such a study of them as would place a greater value upon his services when a greater development the more important. China furnishes about 5 per cent of the total tin production of the world, the center of production being in the Mengtze district, Province of Yunnan, the Kochiu mines worked by native methods being 30 miles from Mengtze. The Yunnan Syndicate (Ltd.) and Société d'Exploitation de Ling Ngan have headquarters at Yunnan.

The chief center of antimony production is the Iyang district in Hunan. The operating concerns are the Pao Hua Co., Yunnan; Szeching mines, Kuangsi; and the Hua Chang Antimony Refining Co., Changsha (Hunan).

Where foreign mining engineers are being employed they have usually been of the nationality of the capital.

Tayeh Iron Mines, owned and managed by the Han Yeh Ping Iron & Coal Corporation (Ltd.), Chinese, Hankow. These mines supply the ore for the Han-yang Iron Works, China's large iron and steel plant.

Tung Kuan Shan Mines, above Wuhu, Anhui Province. A concession to a foreign syndicate to work these mines was surrendered in 1910 to a Chinese company forming for their exploitation.

The chief deposits of copper are those of Yunnan, Szechwan, Anhui, and Kansu. Its mining has been rigorously controlled by the Government, copper being an important medium of currency.

Government smelting works at Yaokai, Kansu. In charge of British engineer, with Belgian and Spanish assistants.

Government mines at Chang Pailing, Kanchow, Kiangsi Provinces. Worked by native methods.

Government mines at Pai Shui Ho, Penghsien, Szechwan. Japanese assayists.

Government mines in Huilichow, Szechwan.

Of the other minerals mined, tin and antimony are

of such resources might come about. Such positions are very few, however, and I know of no openings. Such positions would usually come under the Ministry of Education, Peking; instructors, however, are usually employed through educational missions abroad, Chinese officers abroad, or through the faculties of foreign universities at the instance of Chinese officials or former students returned to China. Mining matters in China come under the Ministry of Commerce and Industry, Peking.

THE RADIO ACTIVITY OF COLORADO CARNOTITE.

By FRANK C. PERKINS.

At Telluride, Colo. and at other places in the famous Paradox Valley of Southwestern Colorado, the radio mineral carnotite is found as well as the uranium vanadium ores and the photographs made with this material are most interesting. The writer is indebted to Mr. O. Barlow Willmarth for these illustrations and data of the material.



Photographs Made by Exposure to Mineral Carnotite.

It is stated that the photographs are the result of various exposures of the crude shipping ore as mined with the chemical concentrate. At Telluride, San Miguel County, Colorado, there have been on exhibition some remarkable photographs produced exclusively by the light from carnotite. The most remarkable photograph is said to be the one produced from such radio active rays emanating from a small cake of chemically concentrated carnotite and which concentrate consists of the uranium element of the carnotite ore.

It is pointed out that the important feature connected with this new method of concentration is the fact that the radio activity of the uranium is not destroyed and apparently is not effected by such concentration formula. This concentrate was from a low grade of carnotite ore. The barrier to such a concentration has previously been that ore buyers claimed as a reason for refusing to consider a chemically con-

centrated uranium product that the radio-activity of the ore was thereby destroyed.

It is held that there is a vast amount of low grade carnotite ore in San Miguel and Montrose counties on the borders of the Dolores River and any satisfactory method of concentration, which means that it must be commercially feasible, will mean added life to the rapidly developing industry of that portion of the southwestern part of Colorado.

One of the accompanying illustrations was taken by the rays from a specimen of high-grade carnotite ore which assayed 49.60 per cent uranium and 19.39 per cent vanadium oxide in the crude state. The plate was steadily exposed in a dark room for about ten hours and it shows the remarkable penetrating power of the radio activity contained in this ore.

The other illustration is the result of a twelve-hour exposure without the construction of the hard rubber slide or other resistance, the Yale key having been placed directly on the photographic plate and the carnotite ore specimen having been placed directly on top of the key for the twelve hours mentioned.

IRON AND STEEL PRODUCTION AND IRON RESERVES.

A report on the extent of the iron-ore resources of the world was presented at the Eleventh International Geological Congress at Stockholm in 1910, in which it was estimated that the total actual resources of iron ore existing in deposits that can at present be worked at an economic profit amount to 22,408,000,000 long tons, representing 10,192,000,000 tons of iron. This total would supply the requirements of the world for considerably less than two centuries, even were the present rate of output not exceeded on the average. The actual resources of the principal ore-producing countries are estimated to be, in the United States, 4,258,000,000 tons, the equivalent in metallic iron being 2,305,000,000 tons; in Germany and Luxemburg, 3,878,000,000 tons, estimated to yield 1,360,000,000 tons of metallic iron; in the United Kingdom, 1,300,000,000 tons, equal to 455,000,000 tons of metal; in France, 3,300,000,000 tons, equal to 1,140,000,000 tons of metal:

and in Spain, 711,000,000 tons, equal to 349,000,000 tons of metal.

In addition to these quantities, which are stated in the report to exist in present workings, the potential resources of the world not yet developed are estimated to amount to 123,377,000,000 tons of ore, representing 53,136,000,000 tons of iron. Further, very large supplies of iron ore are understood to exist in China, Canada, and other countries, but no definite information is at present available as to their extent.

According to a report in the British Board of Trade on iron and steel complete particulars in regard to the output of iron ore in 1912 are not yet available, but it may be estimated that the output in the 10 principal countries dealt with in this return exceeded 146,000,000 tons, and if the minor producing countries be added, it is probable that the world's total output in 1912 was about 152,000,000 tons. The world's output in 1911 was about 5 per cent below that of 1910, but the figures so far available indicate that the output in 1912 was more than 5 per cent above that of 1910. The principal producers were the United States, Germany, France, the United Kingdom, and Spain, in the order given, these countries producing about six-sevenths of the total output of the world.

The quantity of pig iron produced in the world in 1912 may be estimated at 72,000,000 tons, the principal countries of production being the United States, Germany, and the United Kingdom, in the order named, which together account for about seven-ninths of the world's output.

The iron ores used for smelting are of varied chemical composition and occur in several different geological formations. They are also of very different richness, the quantity of iron they yield ranging from as little as 20 per cent to over 65 per cent of their weight. The figures of tonnage of iron ore produced do not, therefore, represent the relative amounts of iron to be extracted.

The statement in Table I shows in long tons the output of iron ore and pig iron in each of the principal countries in which the ore is mined, or in which the smelting of iron is an important industry, in each of the years 1910-12, the figures for 1912 being provisional.

TABLE I.

Countries—	Iron ore.			Pig iron		
	1910. Tons.	1911. Tons.	1912. Tons.	1910. Tons.	1911. Tons.	1912. Tons.
United States.....	a56,890,000	a43,877,000	a55,150,000	27,304,000	23,650,000	29,727,000
Germany (including Luxemburg)	28,248,000	29,399,000	32,190,000	14,556,000	15,324,000	17,582,000
France	14,371,000	16,372,000	b18,744,000	3,968,000	4,398,000	4,870,000
United Kingdom	15,226,000	15,519,000	13,790,000	10,012,000	9,526,000	8,751,000
Spain	8,528,000	8,633,000	(c)	367,000	402,000	(c)
Russia (excluding Finland).....	5,650,000	6,882,000	b 8,051,000	2,983,000	3,526,000	4,119,000
Sweden	5,464,000	6,055,000	6,593,000	594,000	624,000	689,000
Austria-Hungary	4,460,000	4,640,000	d 2,880,000	2,011,000	2,081,000	d1,732,000
Canada	232,000	188,000	156,000	e 715,000	e 819,000	e 906,000
Belgium	121,000	148,000	165,000	1,822,000	2,013,000	2,264,000

a Iron ore sold for paints excluded.

b Partly estimated.

c Not available.

d Austria only; compared with 2,721,000 tons of ore and 1,570,000 tons of pig iron in 1911.

e Exclusive of output of electric furnaces making ferro products.

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NOTES AND COMMENTS.

Adulteration of Olive Oil.

The U. S. Consul at Leghorn, Italy, in a recent consular report, states that treated inferior olive oil is produced in Italy at Porto Maurizio. The oil sells at \$13.77 per 100 lbs. Oil prepared at Nice sells at \$14.54; at Marseilles, from \$11.84 to \$12.11.

Some of this oil is received at the free port in Leghorn and pays no duty. It is there alleged to be mixed with Lucca oil and the whole sold as pure Lucca olive oil. Some is said to be taken direct to Lucca and other places in this district and mixed with genuine Lucca oil and the whole put out as grown in Tuscan and manufactured in Lucca.

The duty and other charges make it cost \$1.58 to \$1.75 per 100 lbs. in addition to the selling price noted, but the mixture is then sold for less than that at which pure genuine Lucca oil can be sold. Treated oil from Porto Maurizio pays no import duty.

An effort to find the quantity of treated oils brought into this district from Porto Maurizio was unsuccessful, but one dealer says that it has reached 2,200,000 lbs. already this season (Feb. 26, 1914).

The Tuscan olive crop for 1913-14 is reported by

growers to be not to exceed one-third of a normal crop. The average annual production for the years 1909-1912 was 158,400,000 pounds.

An authority on oil production here says that 100 lbs. of olives will produce 7.70 to 8.20 lbs. of oil on the first and second pressings. These have been the only oils heretofore considered fit for human consumption. This would indicate a production of about 12,000,000 lbs. of oil. At least one-third of the production is consumed in Italy, leaving 8,000,000 lbs. of pure Lucca oil for export. The exports to the United States during 1913 were 10,292,000 lbs., of which one-third was in the last quarter of the year and from 1913-14 crop. Approximately 2,200,000 lbs. have been shipped already this year (up to Feb. 26).

It would seem that more oil is being sent to the United States as Lucca or Tuscan olive oil than the district produces for export. The treated oil is difficult to detect, but expert tasters allege that they can recognize the mixed oil from the flavor and the effect on the throat.

An effective way to protect the United States from the adulterated oil, if it cannot be detected by chemical examination, would seem to be to have an expert on the ground to see that Lucca oil intended for shipment to the United States is not mixed with the deodorized oils or other inferior oils and to place an identification mark on each container before exportation.

Development of British Columbia Coal Field.

The prospective opening of the Panama Canal has given impetus to various industries, activity to plans for opening new mines, and the development of the natural resources of British Columbia. This is especially true in regard to the coal-mining interests of the Province. The following notes on the British Columbia coal are taken from a Daily Consular and Trade Report:

It is announced that Mr. D. A. Thomas, the Welsh coal magnate, who is now on the Pacific coast, has secured options on the anthracite coal lands controlled by the British Columbia Anthracite Syndicate, a company composed of Quebec financiers, in what is known as the Groundhog district in British Columbia and estimated to contain 1,141,444,000 tons. In addition to the coal deposits the company holds charters from both the Dominion and Provincial Governments for constructing a railway from the mouth of the Naas River into the coal fields, a distance of 140 miles, and beyond its holdings for a distance of 60 miles.

The product in the Groundhog district is said to be the only hard smokeless steam anthracite coal in the world outside of Wales, Pennsylvania, and West Virginia. The opening of the Panama Canal will enable naval and other vessels using hard coal to come through the canal with a small amount of fuel in their bunkers and replenish their supplies at one of the Pa-

cific stations with coal from the British Columbia mines.

Nasoga Bay, the port for the proposed railway, is said to be admirably adapted for a coal-distributing point, the harbor being well protected and capable of berthing large vessels. The estimated cost of building a railway into the coal fields, equipping the colliery, providing rolling stock, buying coal-carrying ships, and general organization on a working basis is \$10,000,000.

Engineers who have surveyed the Groundhog district report that sufficient coal could be mined from the field to supply all the naval squadrons on the Pacific Ocean with smokeless anthracite coal, and that on account of its geographical location a port at the mouth of the Naas River could compete with the Welsh and Pennsylvania collieries.

Nasoga Bay is closer to the Orient and to Russia than any other sheltered harbor on the Pacific adjacent to a supply of smokeless coal, and is therefore more suitable for a coal-distributing center, and it has the advantage of an almost unlimited supply of this valuable fuel not far from the port, which would facilitate transportation to Hongkong, Yokohama, Vladivostock, Australia, New Zealand, and other naval bases in the East.

Progress In Artificial Silk Manufacture.

According to the European press, the Fabrique do Soie Artificiele de Tubize, the leading Belgian Company, which has hitherto manufactured by the gun-cotton process, is increasing its capital by \$380,000 in order to acquire a controlling interest in a new company which will work the viscose system in Belgium. The report now issued shows a net profit of \$209,000 against \$265,000, and dividends of 25 per cent on the preference shares and 20 per cent on the ordinary shares are being paid. The report issued by the Vereinigte Glanzstoff-Fabriken, Elberfeld, probably the largest producers of artificial silk in the world, shows a net profit of \$1,367,000 against \$887,000 in the previous year, and a dividend of 34 per cent is proposed. Up to about two years ago this company worked only the cupro-ammonium process, but it has since adopted the viscose one, with good results. It has a large financial interest in the British Glanzstoff Mfg. Co., whose works are at Flint.

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INSPECTION ENGINEERING—A NEW PROFESSION.*

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"This is an age of specialization" is a statement almost as old as the further statement that "electricity is in its infancy." It is furthermore every whit as true and both are coming more and more into evidence. A score of years ago electrical engineering was considered merely as a branch of mechanical engineering; today it is not only a science in itself but has in fact its branches.

From these two sciences is gradually developing what may be termed inspection engineering. There have of course been contributing factors; yet, from the two mentioned, it is receiving its greatest impetus towards a full fledged profession.

In almost every engineering industry, one finds nowadays that among the various duties of the force, inspection both of the raw and of the manufactured products, forms no small item. Likewise, if one examines into consulting engineering, it will again be found that inspection occupies a very considerable portion of the day's work. Moreover, there have been established throughout America as well as Europe, inspection bureaus, testing laboratories or the equivalent for the purpose of inspecting and testing materials and apparatus of one sort or another, and where the services of experts can be obtained, as desired, by the public at large. It may in consequence be taken for granted that in these days of keen competition and close scrutiny of expense, there must be a real demand for engineering of this kind or it would not exist, to say nothing of its steady expansion.

Viewing a little more in detail the work of consulting engineering, it will be evident after a moment's consideration, that a consulting engineer must not only know in a general way, the various manufacturers of materials and apparatus in his line; but he must be sufficiently well acquainted with such goods, as to be able to measure their relative worth and merit. Otherwise he would not be in a position to advise his clients in the first place what is necessary for their needs; or, subsequently what to select of the goods offered. Furthermore, he must be so thoroughly fa-

miliar with methods of inspection and testing as to insure his clients obtaining after purchasing, materials or apparatus which are in accordance with specifications. This naturally implies a wide practical experience only to be secured from an extended period of actual contact with materials or apparatus of the kind in question; in other words, the consulting engineer must be first an inspection engineer before he can properly qualify for consulting engineering.

Turning now to an equally brief consideration of inspection bureaus or testing laboratories, their staffs, it is obvious, must embrace among others, both consulting and inspection engineers along various lines depending upon the fields of activity covered. Neglecting the research work undertaken by such firms, their general purpose is to hold themselves available as inspectors and testers for anyone choosing to make use of their services; sometimes for consumers, as often for manufacturers. In the former case, the reliability and high grade of the particular materials and apparatus inspected and passed by them are thus assured, while in the latter case the standard of the product as to quality is guaranteed. Not only therefore, are such firms of the greatest assistance to consumers; but, to small manufacturers particularly, they are a decided asset over and above the expense incurred in employing them. It will be appreciated that with ever increasing competition and more rigid requirements to be met than formerly, selling prices are lower and the expenses incident to production, are greater than ever before. Hence, the absolute necessity of making certain that materials and apparatus will be of proper quality when shipped, so that there will be no subsequent allowances to make for defects, thus reducing the already none too large profits. But to create and develop an inspection force, which would in large measure insure such quality, involves comparatively large initial as well as constant maintenance expense, thus placing this form of protection without the bounds of consideration by many, particularly the smaller manufacturers. The establishment of inspection bureaus with fully developed staffs, nevertheless enables many manufacturers to secure adequate inspection of their products whenever an accumulation of stock warrants, and this it will be observed without incurring any expense other than for

*From the Sibley Journal of Engineering.

the actual time of employment of such inspecting force. Again, the placing of recognized inspection labels or stamps on such inspected goods advertises them to prospective customers as of superior quality to similar, unidentified goods and thus several most desirable features are attained, among them a guarantee of high quality of output and excellent advertising for the manufacturer; a feeling of confidence and security on the part of the customer.

It is, however, in connection with large manufacturing establishments that the extent to which inspection engineering has been developed, is best observed. Taking therefore the Westinghouse Electric & Manufacturing Co. as representative in this respect, its inspection department is nominally made up of several hundred inspectors under the supervision of a chief inspector with his aides, whose duties consist in a careful inspection of all raw materials received into the works as well as of all materials in course of manufacture. In reality, however, there should be included representatives of the various branches of the Engineering department who render incalculable assistance at all stages, and the testing department, as well as the road engineers who supervise the erection and test of the finished apparatus at destination preliminary to its acceptance by the customer. Additionally, help is also obtained by employing as occasion makes necessary, outside inspection firms or bureaus to which reference has already been made, for the inspection of certain items purchased, perhaps at a considerable distance from the works, and when the dispatching of a number of the regular works' inspection force would be a matter either of great inconvenience or of excessive expense.

The pioneer inspecting may be considered as being done by the research engineers who prepare specifications covering the required characteristic of the various raw materials entering into the construction of the apparatus, these being used both by the purchasing department in the placing of orders for such materials and by the inspection department in the inspection of them when received; these engineers also standardize existing shop processes as well as assist in developing new ones for the guidance of the manufacturing departments, thus insuring the building of the same class of apparatus in the same way every time. The amount of research and original investigation frequently involved in work of this kind, would hardly be appreciated by any one who is not intimately acquainted with it. Without attempting to enter into details, it may be said that in the preparation of these specifications, every effort is made to adhere as far as possible, to commercially standardized materials and processes, not alone because of the decreased cost connected therewith but on account of the ability to obtain materials more quickly, as well as because such materials are much more likely to be uniform in quality.

As the apparatus passes through its different stages of construction, reliance is placed by the shop men

aside from their experience, very largely upon the working drawings prepared by the designing engineers, which therefore, must be quite complete in the amount of information given. At the same time the designs should be thoroughly practical as against purely theoretical, commercial materials in commercial sizes being specified with common sense limits within which the materials should be worked and the apparatus built. To accomplish this successfully, the designing engineers must be well acquainted with the equipment of the shop in regard to tools, skilled mechanics, adequate inspection and proper supervision. They must therefore, be in exceedingly close touch with actual manufacturing and such being the case, they form an extremely important adjunct to the regular inspection force.

Where a few years ago inspectors were in perhaps the majority of shops of mediocre ability and looked upon as unmitigated nuisances by the workmen and with a feeling of skepticism, even by the management under whose authority they were placed, conditions have of late years changed markedly. None but the very best workmen are now chosen for such positions, with the result that the workmen are glad to have their aid in checking work as it progresses towards completion, since they are thus assured of its accuracy. From what has been said it is readily inferred that every inspector must be a good workman in his line; but, it does not necessarily follow that the converse of the proposition is always true; as a matter of fact, it is not. Besides possessing judgment in the inspection of the work itself, inspectors must have the ability to deal impartially with the workmen with whom they are brought into contact, showing no favors, yet lending a helping hand to all who need it by timely suggestions and encouragement, thus acting as invaluable aids to the foremen. Such qualifications are not easily found in a single individual, so that the selection of competent inspectors is a difficult task and one that may be said to be endless; for the ability of an inspector to fill his position successfully, makes him in due course, eligible for a foremanship.

The testing department, consisting as it does almost wholly of engineers, is generally the last and perhaps the strongest barrier in the shop against imperfect apparatus; and, unusual indeed must be the defect that succeeds in passing all the tests and examinations to which the average piece of apparatus is subjected.

In some cases, especially when very special requirements are to be met, customers like the navy department for example, have their own inspectors present, either during the entire course of construction or else at the testing of the apparatus before shipment, so that an additional safe guard is thus introduced.

The final inspection and test occurs usually at destination when the apparatus is given a run under regular operating conditions, representatives both of the manufacturer and the customer being present. The

successful passing of such tests means the acceptance of the apparatus by the customer and the release of the builder from further obligation except as contracts may have in them certain clauses dealing with the possible subsequent development of defects due to imperfect design, workmanship or material.

In the preceding, only the barest outline has naturally been given of the work of inspection; but, it is hoped enough has been shown to indicate the growing importance of this field of activity and to warrant the statement that inspection is fast becoming a profession in itself.

GAS INVESTIGATIONS OF THE BUREAU OF STANDARDS.*

By MR. R. S. McBRIDE, Associate Chemist, Bureau of Standards.†

It is a pleasure to comply with the request of the editor of this journal for a review of the work of the Bureau of Standards on those problems which are of interest to the gas engineer. It is appreciated that it is only possible to get results of value to the industry and of service to the public, if the investigations are carried out properly, and to plan the work to this end the suggestions and criticisms of those active in the engineering field are of great value. It is hoped that a review of this sort will bring to the bureau many helpful comments.

It is not necessary to go at length into the history of the work now being done at the bureau in the line of standards for gas service, and standard gas testing methods, since most of the readers of the *Journal* are, no doubt, already more or less familiar with Circular No. 32, and with the work which led up to the preparation of Circular 48, "Standard Methods of Gas Testing," the latter now in press. However, it may be well to summarize these with the other phases of the work, in order to show the present status of each of the major branches of it. For convenience of discussion, the problems may be grouped under the following subjects:

1. Specifications for gas quality or service.
2. Gas testing methods.
3. Problems of gas manufacture and distribution.
4. Utilization of gas.
5. Properties of gas.

Service Specifications.—As long as there are a large number of states and cities engaged in regulating the quality of service rendered to the gas customers within their respective limits, there will be great differences both in the form and substance of the regulations adopted; and, even if all the gas companies of the United States were under the control of a single regulating authority (a condition not at all probable even for the future) many differences in the regula-

tions would necessarily remain in order to adapt the specifications to local needs. Nevertheless, there are many fundamental principles uniformly applicable through the country; and in any case the consideration of what has been done elsewhere is a helpful preliminary to the adoption of rules applicable to a given locality.

Following out this idea, the bureau undertook a compilation of all of the rules and laws in force under city or state authorities, and has endeavored to study, not only the regulations themselves but, also, the general results of enforcement, in so far as these results could be learned by correspondence or conferences. The information thus collected formed the basis of the discussion and recommendations of Circular No. 32, on "Standard Regulations for Manufactured Gas and Gas Service."

In these investigations the bureau has endeavored to define the principles which should be the basis of a gas service specification, in order that the local authorities might have conveniently available the net results of the experience of all. And since the circular was prepared with the co-operation of a considerable number of engineers, experienced in the manufacture and distribution of gas, as well as those correspondingly active in state or city work, it became an expression of the best opinion of the industry.

Based, as it is, upon current opinion and practice, the circular requires frequent revision. The second edition is already exhausted and a third is now in preparation. In each edition it is the aim to correct and improve the circular, and to this end suggestions from those interested and experienced in the gas business are always welcomed.

In the utilization of the suggestions of the circular by states and cities, the bureau has been asked to give assistance by sending a representative to attend conferences preliminary to the adoption of rules, or by rendering a report on the proposed regulations. In this work, of course, suggestions from the bureau are purely advisory, and the companies are always left, as they should be, in direct relation with the local authorities. Furthermore, the bureau has endeavored always to make it clear that such suggestions and reports as may come from it are made for the companies as well as for the officials; and in many cases the reports are transmitted to the company at the same time as to the city or state authorities.

Gas Testing Methods.—In the enforcement of regulations, as to quality of gas or gas service, the testing methods must be correct, otherwise friction or serious controversy will sooner or later result. Many examples could be cited where the failure of an inspector to fully understand his testing methods has resulted in such unfortunate incidents. It is clearly desirable, therefore, to have methods applicable in American practice which can be taken as standard; and the formulation of the operating directions for such procedures has been an important part of the work of

*From The American Gas Light Journal.

†Published with the permission of the Director, Bureau of Standards.

the bureau. In many cases extended researches have been needed before recommendations could be made, and it is only recently that these have been collected in the form of a single publication which will be known as Circular 48, entitled "Standard Methods of Gas Testing." This circular will be reviewed in greater detail in the near future. Suffice to say here that it covers the question of methods suitable for the determination of heating value, candle power, and purity of gas (hydrogen sulphide, sulphur and ammonia), the taking of pressure records and the testing of gas service meters.

The methods recommended are in most cases already used in some laboratories, either exactly or in similar form, but in many cases important precautions are emphasized, which are too often overlooked. To follow the correct procedure is rarely difficult, and almost never seriously time consuming; to use a less exact method is, therefore, unnecessary and often inexcusable.

As the work of the bureau in this line is continued, it is proposed to establish what might be termed a laboratory inspection service. This service would consist in an inspection of the apparatus and methods in use in any laboratory, to be made by a representative of the bureau on request; the object being to discover any irregularities in the apparatus or methods employed, and to assist the inspector in charge of the laboratory to correct or eliminate conditions that might lead to incorrect results. In a few cases work of this sort has already been done, not only for the city and state officials, but also in company laboratories. The outcome has been very satisfactory in each case. Where errors were discovered they were eliminated; where no irregularities were noted there was added confidence in the results and satisfaction in the fact. In one or two cases it has been possible to point out the causes of discrepancies previously noted between tests made by the company and those made by the inspector. Causes of friction have thus been removed.

One advantage to the bureau in this inspection service is the familiarity it gives with field conditions, and testing methods recommended will in consequence more likely be practicable and suited to the routine inspection and the works' laboratory.

The proper interpretation of results obtained in the testing of gas is not always easy, even when the methods of testing are known to have been accurate. It is hoped that the discussions of such problems, which are included in the circulars on testing methods and standard regulations, will assist in this interpretation.

Gas Engineering Problems.—It is not necessary for the bureau to go into a detailed study of all the problems of gas engineering, but some consideration must be given to them, in order that the rules proposed and the testing methods recommended may be of a practical nature and applicable under existing conditions. It has, therefore, been necessary to give careful attention

to the difficulties commonly met in manufacture and distribution, and their effects on the service or the gas quality, and the means taken to prevent and overcome these troubles. As more information of this sort becomes available to the bureau, the value of the work done is certain to increase.

As examples of the questions on which there is need of a large amount of work, and to which time will be given as opportunity offers, the following may be cited: What is the effect of different methods of handling, and of different conditions in the works and in distribution, upon the quality of the gas; for example, distribution losses, condensation losses, etc.?

What is the limiting and what the most desirable quality (from standpoint of engineering efficiency) of gas under the different conditions to be met—of kind of coal or oil, of character of process, of local weather and other conditions?

Such questions as these can never be considered as finally settled, for most of them are affected by every important development of the industry. However, their careful consideration cannot fail to give some results of value.

It has also been frequently suggested that the bureau take up the question of collecting and collating gas engineering data of importance to regulating and operating officials. This has not yet seemed practicable, but it is certain that such a collection would be very useful in showing what is standard practice and what variations are likely to be met under special conditions. Each company could then by comparison more readily determine in what particular it could expect to make improvements. Such data should be presented in the form of summaries, which would not subject the individual company to unfair comparisons.

Utilization of Gas.—The work which has been done by the American Gas Institute and the National Commercial Gas Association upon gas consuming appliances has almost wholly dealt with specifications as to the quality of material entering into their construction or with the form of appliance from the standpoint of efficiency or durability. This has left two important phases of the subject which have been taken up only at intervals, generally by some particular gas supply or gas appliance companies: (1) The question as to the proper installation of the appliance from the standpoint of safety from fire and asphyxiation (either due to leakage or to improper combustion); and (2) the question as to the relative usefulness of gases of different kinds or of different heating values. The effect of changing conditions of gas supply upon the efficiency or safety of an appliance must also be considered. Changes of gas pressure, gas density, or the relative amount of air required for combustion are important factors, and very little work has been done to determine the magnitude of their effect.

None of these investigations has been actively taken up by the bureau, but it is hoped that, as information of importance bearing on these questions becomes

available, it can be collected and prepared in a form which will be of value to the company and consumer. The importance of these considerations, as affecting the choice of regulations for service, will be clear to everyone; the necessity for the bureau to give some consideration to the problems is, therefore, apparent.

Properties of Gas and Gas Analysis.—The preparation, free from impurities, of all of the constituent gases of ordinary manufactured gas, has been undertaken by the bureau in order that the properties of these gases may be more exactly determined. It is expected that the heat of combustion, specific heat, density, refractive index, solubility and other important chemical and physical constants will be determined.

After these constituent gases are available it will be possible to make up known mixtures of them, and work by gas analysis methods commonly used can then be carried out in ways not previously done. This is of importance because of the commercial applications of gas analysis as well as its scientific interest.

At the present time there are no methods for the exact separation of the various unsaturated hydrocarbon gases commonly called "illuminants." These are the most important of the heat-giving and illuminating constituents of commercial gas, and yet we have no means of separating the several groups of gases thus classed together, much less the individuals of each group. Preparation and testing of mixtures containing known quantities of these compounds will throw much light upon the subject and perhaps will make it possible to devise analytical methods for their determination.

The commercial types of gas analytical apparatus are generally only simplified forms of the more accurate types of equipment, accordingly the investigation of the exact methods will show what changes, if any, are needed in the ordinary types.

Special gas analytical methods are needed from time to time; for example, methods for quick and accurate determination of the carbon monoxide content of air in appliance testing, the determination of carbon dioxide in air for ventilation tests, or special analysis of gases evolved in various processes. Some of these require special investigation, others can be adapted from the methods applicable to illuminating gas.

Reactions and Properties of Gas Mixtures.—As soon as gases of known composition are obtainable, either by mixing pure gases in the desired proportions, or by analyzing to accurately determine the character and amount of the hydrocarbons, it will be possible to carry out tests which will show the effect of temperature and pressure, as well as mechanical treatment and friction of flow, on the composition of commercial gases. Means of elimination of the large distribution losses may then be obtainable, but more than commercial tests on this problem are needed, since the vapor pressure relations are complicated by the solubility of the gases both in gases and in the condensed portions

of the original mixtures. The changes of "vapor pressure of a liquid" with change of the gas over it may be sufficient to be of appreciable effect.

The relation of heating value to composition, or density to composition, will be apparent when the constants of each gas constituent are known; but the open flame and mantle candle power must be determined separately for each mixture studied, since these properties are not additive. The relation of heating value, comburiverous power and density to gas candle power in both open flames and mantles can then be deduced.

Gas reactions of various sorts are of great manufacturing interest, and with a supply of pure gases they can be studied. The thermal decompositions and interactions of the hydrocarbon gases have been little studied, but facilities should be available, permitting work to be done in this line.

Heating Value Standards.—The heating value of a gas is the most important gauge of the quality for domestic or industrial use, and hence this property is rapidly becoming the basis for the fundamental specification of quality. To fix it at the proper value is important, for too high a requirement gives rise to unduly expensive gas, while too low a figure permits qualities which, though cheaper in cost per 1,000 cubic feet, are really more expensive in giving less heat per dollar of cost to the user. To fix the proper intermediate value, or range of proper values, is not an easy task; but the rational method to apply in the estimates of this value can be clearly defined. The bureau has undertaken an investigation of this problem, with the idea of clearing up some of the uncertainties which now exist. This study will be directed toward the establishment of certain principles which should guide an engineer in his estimates on this subject; but we shall not, of course, attempt to lay down any rule which could be followed in every case, much less any formula in which the several factors could be entered and a calculation performed to give the desired result. The advantages which may result from a full consideration of the subject, and from the use of the method by others in actual practice, are the following:

1. The basis of heating value regulations should be made clear.
2. Regulations would be based on technical considerations, not the arbitrary opinion of any person or body of persons.
3. The customer would get his service on the most economical basis; that is, the company would have a proper return upon its investment at the least expense to the public.

4. A company would have well defined means of showing whether changes of standards were required.

These advantages show that the standard could be made fair and equitable, and sound, both from economic and engineering viewpoints.

Completed Researches.—In the above discussion many of the plans for the future have been suggested,

as well as outlines of present work given. As a brief statement of some of the investigational work which has been completed, we may give the following list of publications of the Bureau already issued or now in press:

"Industrial Gas Calorimeter" (Technical Paper, No. 3; in press).

"Determination of Sulphur in Illuminating Gas" (T. P., 20).

"Determination of Ammonia in Illuminating Gas" (T. P., 34, in press).

"The Pentane Lamp as a Working Standard" (Scientific Paper), 216.

"Standard Methods of Gas Testing" (Circular 48, in press).

"Standard Regulations for Manufactured Gas and Gas Service" (Circular 32, out of print. New edition in preparation).

"Legal Specifications for Illuminating Gas" (T. P., 14, out of print, superseded by Circular 32, 2d edition).

These reports, and those on other investigations which do not have to do with the gas itself, but are of interest to gas engineers, may be had on request. A complete summary of them is given in the list of publications of the Bureau (Circular 24).

In carrying out these investigations the Bureau has striven only to serve as a clearing house for information and as a co-ordinating agency with reference to the many sources of opinion and information among the companies and the various states and cities. The Bureau is entirely without authority or desire to act as a regulating agency; it will continue to serve only as a medium of exchange for technical information and will consider local problems only in an advisory capacity. The work of the Bureau should be of great assistance also to consulting engineers by tending to make their work more satisfactory, and to increase the demand for the services of well qualified engineers.

In the work outlined above progress will, of course, be slow, partly because of the magnitude and difficulty of the problems, partly because of the limited resources of the Bureau. If the cordial co-operation of city, state and company officials is accorded the Bureau, in the future as in the past, substantial progress will, however, be made in the study of these problems.

The German demand for the various classes of imported stock foods continues to be enormous, and is stated by Dr. Waage, the director of the Union of German Wholesale Dealers in Fertilizers and Fodders, to amount to 30 per cent of the entire requirements of the Empire. This informant fixes the annual consumption of all stock foods at 23,300,000 tons, of which 16,700,000 tons is of domestic production.

ALUM IN FOODS.*

A report on the influence of aluminum compounds on the nutrition and health of man has been submitted by the Referee Board of Consulting Scientific Experts, in answer to questions put to it by the department. The report of the board itself, signed by each member, is brief, but it is accompanied by three elaborate reports giving the results of three sets of extensive experiments on human subjects conducted independently by three members of the board. To get the board's conclusions before the public at this time, it is considered advisable to publish its findings, but to omit the extensive reports of the three experiments, giving only their final conclusions.

The questions submitted to the board were as follows:

1. Do aluminum† compounds, when used in foods, affect injuriously the nutritive value of such foods or render them injurious to health?

2. Does a food to which aluminum compounds have been added contain any added poisonous or other added deleterious ingredients which may render the said food injurious to health? (a) In large quantities? (b) In small quantities?

3. If aluminum compounds be mixed or packed with food, is the quality or strength of said food thereby reduced, lowered, or injuriously affected? (a) In large quantities? (b) In small quantities?

In order to base their report upon first-hand knowledge, the board instituted three sets of experiments, each independent of the others. One set of experiments was conducted by Dr. Russell H. Chittenden, of the Sheffield Scientific School, Yale University, New Haven; another by Dr. Alonzo E. Taylor, of the Medical School of the University of Pennsylvania, Philadelphia; and the third by Dr. John H. Long, of the Northwestern University Medical School, Chicago. In each case tests were made on healthy young men by including aluminum in some form in their food. The food was all carefully measured and weighed and the amounts of its principal ingredients were determined by analysis. The excretions of the men's bodies (both urine and feces) were carefully collected, examined, and analyzed. Daily records of body weight, temperature, respiration, and pulse were kept for each man, and notes were made of any unusual symptoms. Any disturbance in health or physiological processes was thus detected.

Each experiment included three periods, in the first and last of which no aluminum was administered. During the middle period aluminum compounds were administered, the "dose" increasing as the experiment progressed. In this way the effect of large quantities was compared with that of small quantities. In Dr. Chittenden's and Dr. Taylor's experiments some of the men who served as "control" subjects received no

*From Bulletin No. 103 of the U. S. Department of Agriculture.
†Aluminum is a synonym for aluminium, the metal used for cooking utensils and other implements. Alum or sodium aluminum sulphate is a salt of this metal.

aluminum at any time, so that any disturbances due to other causes might be checked up.

Dr. Chittenden's experiments included 12 men and continued from January 15 to June 22, 1912. During 130 days the diet contained bread raised with an alum baking powder made in the laboratory.¹ The dose of aluminum compound was increased from time to time, at first by increasing the quantity of bread and later by increasing the quantity of the baking powder used in making the bread. In this way the alum² used per man per day was increased from 0.578 gram³ (8.920 grains) at the beginning to 2.287 grams⁴ (35.295 grains) at the close of the dosage period; the actual aluminum contained in this dosage ranged from 0.065 gram (1.003 grains) to 0.257 gram (3.966 grains) per man per day. Eight men used the alum bread, while four had no aluminum in their food.

Dr. Long's experiments ran from February 8 to June 7, 1911, and included six men, all of whom received the dosage. Baking powder bread was not used, but instead for 40 days a mixture of the same composition as the residue left in such bread by alum baking powder was administered in the form of a powder in water or milk. For 30 days the quantity of alum used was 2 grams⁵ (30.866 grains) a day for each man; in the next 10 days the dose was doubled. Afterwards for 30 days the baking powder residue was treated so as to wash out everything except the compounds of aluminum with hydrogen and oxygen (aluminum hydroxide), the dose at first being the amount obtained from 4 grams⁶ (61.732 grains) of alum per man per day, which was increased in the second 10 days to 6 grams⁷ (92.598 grains) and in the third 10 days to 10 grams (154.330 grains) of alum. Finally, in a period of 10 days, the dose was the sodium sulphate consumed when 4 grams of alum were used, this compound being the cathartic ingredient which is left in bread by alum baking powder.⁸

¹This bread was made fresh every day and contained in one baking of two loaves approximately:

Sifted flour, quarts.....	2
Baking powder (25 per cent calcined alum), heaping	
teaspoonfuls	4
Salt (approximately one rounded teaspoonful), ounce..	1/4
Butter, ounce	1
Water, sufficient quantity.	

Later in the experiment a greater proportion of alum baking powder was used in the making of the bread in order to facilitate administering larger amounts of alum.

²The term "alum" as used under the heading, "Character of Experiments Conducted," refers to the calcined sodic aluminic sulphate commonly used in alum baking powders and not to the ordinary crystallized alum.

³Equivalent to approximately two-thirds of a level teaspoonful of baking powder containing 25 per cent of alum. All the figures in this and succeeding footnotes must of necessity be approximate, since teaspoons vary in size and baking powders in composition.

⁴Approximately equivalent to 2 3/4 level teaspoonfuls of alum baking powder.

⁵Approximately equivalent to 2 1/2 level teaspoonfuls of alum baking powder. Equivalent to about 0.223 gram (3.44 grains) of aluminum.

⁶Approximately equivalent to 4 1/2 level teaspoonfuls of alum baking powder.

⁷Approximately equivalent to 6.8-10 level teaspoonfuls of alum baking powder. These amounts of alum are equivalent to about 0.44 gram (6.86 grains), 0.67 gram (10.29 grains), and 1.11 grams (17.15 grains) of aluminum.

⁸Editorial note: Sodium sulphate or Glauber's salt is a substance derived from the interaction of alum and baking soda in making bread with alum baking powders and is of itself a cathartic, formerly much used medicinally. Cream of tartar baking powder, when used in bread, by a similar interaction produces a cathartic substance known as sodium tartrate. Phosphate baking powders when used in making bread produce a cathartic substance known as sodium phosphate. Cream of tartar and phosphate baking powders produce cathartics, similar to that produced by alum baking powders, when used in quantities.

Dr. Taylor conducted experiments with a squad of eight men from October 8, 1911, to May 10, 1912, with an intermission from December 16 to January 14. In this case also the powder was not used in bread, but was administered in wafers or dissolved in water. Six of the subjects took the aluminum compounds, while the other two took milk sugar, the men themselves not knowing which they were taking. There were two groups of experiments in which the whole squad took part. In the experiments of the first group, which ran from October 8 to December 16, tests were made with alum alone. The dose at first was such as to give each man 0.1 gram⁹ (1.5433 grains) of aluminum a day and was increased from time to time until the daily dose was 0.298 grams¹⁰ (4.599 grains) of aluminum for each man. The second group ran from January 14 to May 10. Tests were made with the residue from alum baking powder; tests were also made with certain aluminum compounds (aluminum hydroxide and aluminum chloride) which may be found in the residues from alum baking powders of different kinds, and with sodium sulphate, the purgative salt left in bread by alum baking powders. The smallest dose of the compounds containing aluminum gave each man 0.227 gram¹¹ (3.503 grains) of aluminum a day, while the largest dose gave 0.969 gram¹² (14.954 grains) of aluminum a day. The dose of the purgative salt (sodium sulphate), in which there is no aluminum, was 5.23 grams¹³ (80.714 grains) per man per day. Following these experiments four men took 1 gram (15.433 grains) of aluminum a day each for several days,¹⁴ and then their blood was tested to detect any aluminum that might be present in it. No aluminum was found in the blood. As a further indirect test to determine whether aluminum was resorbed, one man took for five days enough aluminum hydroxide to furnish 0.660 gram (10.186 grains) of aluminum a day and another took enough to give 0.540 gram (8.334 grains) a day for five days. The men were fed a diet of low and known phosphorus content and the excrements analyzed for phosphorus, in order to detect, if possible, signs of abstraction of this element from the tissues by resorbed aluminum. This test failed to demonstrate resorption of aluminum.

CONCLUSIONS OF INDIVIDUAL INVESTIGATORS.

Dr. Chittenden concludes from his experiments that small quantities of aluminum compounds, and even comparatively large quantities, when taken daily with the food, have no effect upon the general health and nutrition of the body. "In other words," as he sums up his conclusions, "aluminum compounds when used in foods—as in bread—in such quantities as were em-

⁹Approximately equivalent to a level teaspoonful of alum baking powder.

¹⁰Approximately equivalent to 3 level teaspoonfuls of alum baking powder.

¹¹Approximately equivalent to 2 1/4 level teaspoonfuls of alum baking powder.

¹²Approximately equivalent to 10 level teaspoonfuls of alum baking powder.

¹³About one-fifth ounce of Glauber's salt.

¹⁴This corresponds to approximately 10 level teaspoonfuls of alum baking powder.

ployed in our experiments do not affect injuriously the nutritive value of such foods or render them injurious to health, so far as any evidence obtained in our experimental work indicates."

Dr. Long, in concluding his report, calls attention to the fact that alum is rather generally used in the manufacture of cucumber pickles. This is an old practice which had its origin in the household rather than in the factory and is still common in the household. The hardening effect of the alum is believed to help in keeping the pickles. In the factory the cucumbers are first soaked for several weeks in strong brine, then in fresh water overnight, this process being sometimes repeated. Then the cucumbers are put into an alum liquor in which the weight of alum used is about one-fourth of 1 per cent of the weight of the cucumbers. The cucumbers and liquor are heated up to 120° or 140° F., then cooled and allowed to stand for from 6 to 24 hours. Then comes a bath in fresh water and afterwards the final treatment with vinegar. The vinegar takes out some of the alum from the pickles, so that usually the alum left in them amounts to less than two-tenths of 1 per cent.

Alum is also used in the preparation of maraschino cherries, and perhaps some other fruits. But the quantities of aluminum that might be consumed either in pickles or in the fruits referred to are so small, compared with the quantities actually consumed in baking powders, that the study of alum baking powders may be taken to cover the entire field.

Alum, as such, is not present in the food when eaten. In the process of baking, the alum and soda in baking powder break up and recombine into several compounds. One product is the carbonic acid gas, which does the work of leavening. This gas passes off, leaving in the bread an aluminum compound and a compound called sodium sulphate. Dr. Long concludes that the cathartic action of large residues from the alum and soda combination—for instance, the residue left when the large dose of alum, 4 grams¹⁵ (61.732 grains), was used—must be considered objectionable when administered daily. But this is much above the consumption in actual practice, and amounts of alum not above 2 grams¹⁶ (30.866 grains) a day—a liberal allowance—do not appear to be harmful in any practical sense. Since the quantities of aluminum compounds consumed with other foods are insignificant compared with the quantities consumed in foods prepared with baking powder, the findings from the study of baking powder residues must be held to cover all cases. Keeping in mind that the aluminum compounds actually in the food when consumed are comparatively inert, Dr. Long declares that "it can not be said that, when mixed with foods in the small quantities actually considered necessary, they add a poisonous

or deleterious substance, or injuriously affect the quality of the food with which they are used."

Dr. Taylor's conclusions agree in effect with those of his associates. He says, "We have had, unquestionably, evidences of the catharsis caused by the administration of large doses of baking powder." With the large doses used in his experiments, the stools are increased in weight and frequency, the movements are loose, and colic is apt to attend the evacuations. This condition is the result of sodium sulphate, which, though not an aluminum compound, is a residue of the alum baking powder. But with very large doses of aluminum compounds occasionally dry colic may also be noted.

"I personally," says Dr. Taylor, "do not believe that it would be healthful for anyone, in camp or out of camp, to live upon a diet of baking powder biscuits. I do not believe that the regular ingestion of sodium sulphate in doses of from 3.5 to 5 grams¹⁷ (54 to 77 grains) per day, with the normal diet, resulting in distinct looseness of the bowels, is a procedure to be recommended. Prolonged administration of saline cathartics even in small dose tends to leave behind a condition of constipation; and it is certainly the experience of the medical profession that the practice of the regular administration of saline cathartics is not to be recommended. This aspect of the question is of course not peculiar to aluminum baking powder, but applies to all baking powders, since to a greater or less extent a saline cathartic remains as the residue of the reactions of all known baking powders, as demonstrated in direct tests with different baking powders on human subjects.¹⁸ There is no evidence in our results to indicate that the occasional and ordinary use of bread, biscuits, or cake prepared with aluminum baking powder tends to injure the digestion. The amount of saline cathartic that would be ingested under conditions of normal diet would be very small and would provoke no catharsis or symptoms of any kind."

One other effect of the administration of compounds of aluminum is noted by Dr. Taylor, namely, a distinct decrease of phosphates in the urine and a corresponding increase of phosphates in the stools. But the extent of this change is too slight for it to have any material meaning or effect.

CONCLUSIONS OF THE REFEREE BOARD.

With the results of these independent experiments agreeing so well, the Referee Board were enabled to draw up a unanimous report, signed by all the mem-

¹⁵One-eighth to one-sixth ounce of Glauber's salt.

¹⁶"We must not, however, be oblivious to the fact," says Dr. Taylor, who conducted part of these investigations, "that a saline cathartic residue results from the reaction of every form of known baking powder now commonly employed. The use of cream of tartar or tartaric acid baking powder leaves in the alimentary tract a residue of tartrates which exhibit the action of a saline cathartic and of diuresis (excessive excretion of urine) as well. The so-called phosphate baking powder leaves as a residue of reaction sodium phosphate, again a saline cathartic. And aluminum baking powder leaves as a residue of reaction sodium sulphate, a saline cathartic. Apparently, therefore, at present at least, the use of baking powder is associated with the introduction into the alimentary tract of a certain amount of saline cathartic, the salt differing with the use of the particular type of baking powder."

¹⁵Approximately equivalent to 4½ level teaspoonfuls of alum baking powder.

¹⁶Approximately equivalent to 2¼ level teaspoonfuls of alum baking powder.

bers, namely: Ira Remsen, president of Johns Hopkins University, chairman; Russell H. Chittenden, professor of physiological chemistry in Yale University and director of the Sheffield Scientific School; John H. Long, professor of chemistry in the Northwestern University Medical School; Alonzo E. Taylor, Benjamin Rush professor of physiological chemistry in the University of Pennsylvania; and Theobald Smith, professor of comparative pathology in Harvard University.

In their report the board first defines their understanding of the terms "small quantity" and "large quantity," as applied to alum baking powders, as follows:

By the term "small quantity" we understand such an amount as may be ingested in the normal use of biscuits, pastry, or other articles leavened with baking powder, as these foods are practically used in the ordinary American family. This amount will not average more than 25 to 75 milligrams¹⁹ (0.39 to 1.16 grains) of aluminum daily for the days of consumption of such articles.

By the term "large quantity" we understand such an amount of aluminum as would be ingested only under very unusual conditions, as for example, where the flour consumption is mainly in the form of biscuits or other articles leavened with aluminum baking powders. This amount may reach 150 to 200 milligrams²⁰ (2.31 to 3.09 grains) of aluminum per day. A person subsisting mainly on baking-powder biscuits, as may happen in camp life, might ingest an amount in excess of 200 milligrams per day. With this possibility in mind, we have also studied the effects of amounts up to and exceeding 1,000 milligrams²¹ (15.4 grains) of aluminum per day.

With this understanding of the terms, the board gives the following answers to the questions submitted to them:

Aluminum compounds when used in the form of baking powders in foods have not been found to affect injuriously the nutritive value of such foods.

Aluminum compounds when added to foods in the form of baking powders, in small quantities, have not been found to contribute any poisonous or other deleterious effect which may render the said food injurious to health. The same holds true for the amount of aluminum which may be included in the ordinary consumption of aluminum baking powders furnishing up to 150 milligrams (2.31 grains) of aluminum daily.

Aluminum compounds when added to foods, in the form of baking powders, in large quantities, up to 200 milligrams (3.09 grains) or more per day, may provoke mild catharsis.

Very large quantities of aluminum taken with foods in the form of baking powders usually provoke catharsis. This action of aluminum baking powders is due to the sodium sulphate which results from the reaction.

The aluminum itself has not been found to exert any deleterious action injurious to health, beyond the production of occasional colic when very large amounts have been ingested.

When aluminum compounds are mixed or packed with a food, the quality or strength of said food has not been found to be thereby reduced, lowered, or injuriously affected.

In short, the board concludes that alum baking powders are no more harmful than any other baking powders, but that it is wise to be moderate in the use of foods that are leavened with baking powder.²²

¹⁹This is approximately equivalent to one-quarter to three-quarters of a level teaspoonful of alum baking powder.

²⁰This is approximately equivalent to 1½ to 2 level teaspoonfuls alum baking powder.

²¹Approximately equivalent to 10 level teaspoonfuls alum baking powder.

²²See footnotes, pages 3 and 6.

ALBERTA'S COAL RESOURCES.

According to an annual report issued by the provincial government of Alberta, 289 coal mines in Alberta, employing 6,610 men inside and 2,253 men outside, produced 4,306,346 tons of coal, 130,861 tons of briquets, and 65,167 tons of coke during 1913, an increase of nearly 25 per cent over 1912. Of this output, 1,000,000 tons of coal were exported to other Provinces in Canada and to the United States.

The classification of the output of 1913 is as follows: Bituminous, 2,374,401 tons; lignite, 1,763,225 tons; anthracite, 168,720 tons; used in coke production, 104,012 tons. With the introduction of new capital and the opening of large mines, adequately equipped with American machinery, there is every reason to believe that the exportation of coal will be increased during this and coming years.

It is stated that the tonnage in 1913 would have been much larger but for the extremely mild weather early and late in the winter. The increase of output during the last eight years has been about 500 per cent, the tonnage being as follows since the organization of the Province: 1905, 811,228; 1906, 1,385,000; 1907, 1,834,745; 1908, 1,845,000; 1909, 2,174,329; 1910, 3,036,757; 1911, 3,694,564; 1912, 3,446,349; and 1913, 4,306,346 tons.

Experts estimate that the actual and probable coal resources of Alberta total 1,975,039,000,000 metric tons, or 14 times the reserves of British Columbia, 18 times more than Saskatchewan, and 110 times greater than Nova Scotia, at present the largest producing Province in the Dominion of Canada. The Edmonton district has a coal area of 77,184 square miles of coal fields in Canada.

There are three distinct coal horizons in Alberta: The Kootenay or Lower Cretaceous; the Belly River or Middle Cretaceous, and the Edmonton, lying at the top of the Cretaceous. The upper Edmonton formation covers an area of 24,779 square miles, while the lower Edmonton formation occupies 52,405 square miles.

The Belly River formation in eastern Alberta covers 16,000 square miles, the best coal occurring on its borders, where there are persistent seams. Lignite seams occur at Medicine Hat, Taber, and Lethbridge; it has also been found at Tofield, Calgary, and Edmonton. This series is identical with that at Peace River, known as the Dunvegan.

The geological survey of Canada gives these figures of Alberta's coal resources:

Actual reserves—Anthracite, 668,000,000 tons; bituminous, 3,209,000,000 tons; semibituminous and lignites, 384,908,000,000 tons.

Probable reserves—Anthracite, 100,000,000 tons; bituminous, 194,883,000,000 tons; semibituminous and lignites, 491,271,000,000 tons.

METALLURGY.

NOTES ON METALLOGRAPHY.

By H. B. PULSIFER.

A MICROSCOPE TABLE TO PREVENT VIBRATION.

At the Armour Institute of Technology conditions are not favorable for taking long exposures with the photographing microscope; besides the continual jar in a large building housing many students, the gymnasium is directly above the laboratories used for metallography, a four track railroad passes directly contiguous

pieces. The channels are likewise bolted to stubs on the lower angle pieces. The horizontal angle pieces are 1.5 in. stock. The springs are suspended from hooks let down from the top cross channels and are adjustable by means of the long threaded end raised or lowered by turning the nut. A vital part of the frame is a hundred pounds, or more, of lead fastened beneath and in the center of the channel. The entire weight of the channel, itself, with the microscope, and the weight beneath must amount to over two hundred pounds; this

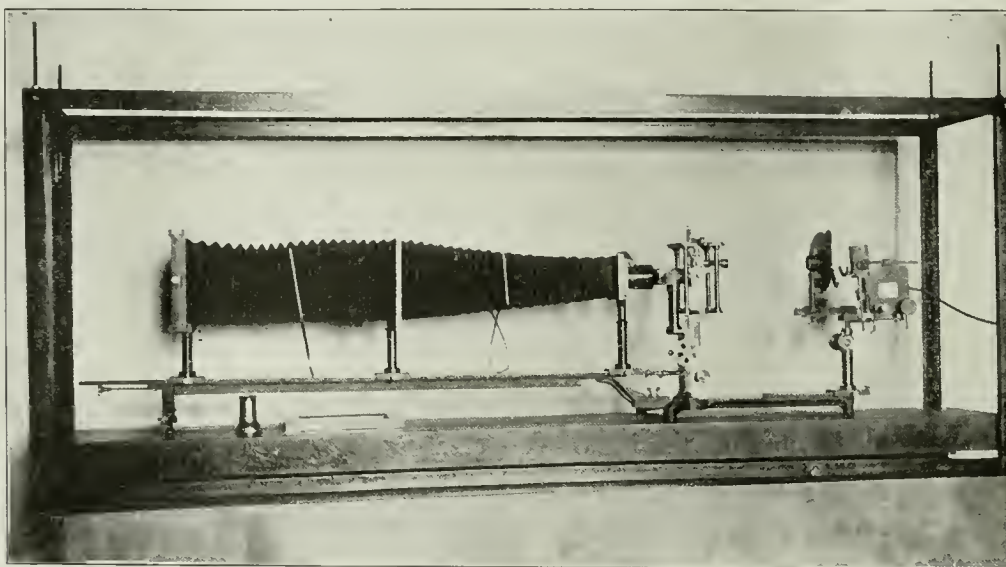


Fig. 1. Jar-Proof Microscope Stand.

to the building while on two other sides heavy teams and trucks continually pass in the street. Every part of the buildings shake with the passing of trains or teams, even special piers deeply bedded independent of the buildings prove no adequate protection against disturbing influences.

The steel frame supporting the bed plate on which rests the microscope, as seen in Fig. 1, was designed for long quiet exposures and has proven satisfactory in use.

Steel springs hung from the four upper corners of the frame carry a 12-in. steel channel bar of standard section; there is sufficient clearance so that shocks and the swaying of the building do not bump the base against the frame. Damping compression springs under the four corners of the channel carry a portion of the load and bring the base to rest quickly when it is desired to make an exposure.

The frame is 6 ft. 4.5 in. long, 2 ft. 6.5 in. high and 14.5 in. wide outside the uprights. The uprights are 1.5 in. channels, beveled at the top and bolted to each side of the angle irons which form the horizontal

gives sufficient inertia so that an image thrown the full length of the bellows is not seen to move on the screen, although the frame may be in violent agitation.

Fig. 2 shows a granule of ferrite separated from contiguous ferrite by a division line which marks strongly with pearlite areas. The magnification is 1,750 diameters and the exposure was 7 minutes long, taken with the building vibrating strongly; without the frame the lines might have vibrated with an amplitude of an inch or so, and the negative been worthless. Most of the illustrations here presented were made under similar conditions with the aid of the shock-proof table.

THE CELLULAR NATURE OF FERRITE.

Ferrite is one of the easiest structural constituents of steel to recognize. A light etching or the polished specimen with picric or nitric acid suffices to throw it into relief against its sorbitic or pearlitic background, the latter usually accompanying ferrite whenever it is found in commercial steels of the carbon range .05 to .70 per cent carbon. Fig. 3 shows just such a case; it is a .40 carbon well annealed machine steel, with the ferrite in small flakes and the pearlite nicely granular,

magnification 1,000 diameters, lightly etched with picric acid.

Although the print shows the structural separation of the ferrite and pearlite there is a further resolving of the ferrite possible. Ferrite in as coarse masses as shown in Fig. 3 can be shown to consist of grains if further and proper etching is applied. The ferrite will be found to be of a granular nature and separated into smaller units by division lines. This is what we term the cellular nature of ferrite; it is not difficult of detection whenever ferrite is present in quantity or



Fig. 2. .13% Carbon Steel x 1750 dia.

whenever the ferrite, originally a constituent of pearlite, unites enough to be called "free ferrite." Needless to say, the metallurgist is always anxious to see this secondary size of the ferrite aggregates. Etching with picric and nitric acids, first with picric in alcohol, then with nitric in alcohol, does not fail to bring the appearance. In a rough way, the more impure the steel the quicker it develops. It was thus developed in Fig. 2.

Fig. 4 is the appearance of Prof. Burgess' electrolytic iron (very pure ferrite) after several minutes etching with both reagents, at a magnification of 200 diameters. As the piece is about 99.97 per cent pure iron it etches slowly and the lines of demarkation are not very broad. Fig. 5 is from the same piece of metal at a point where it ruptured by drawing apart; it will be seen that the grains are not pulled apart nor is the cellular nature

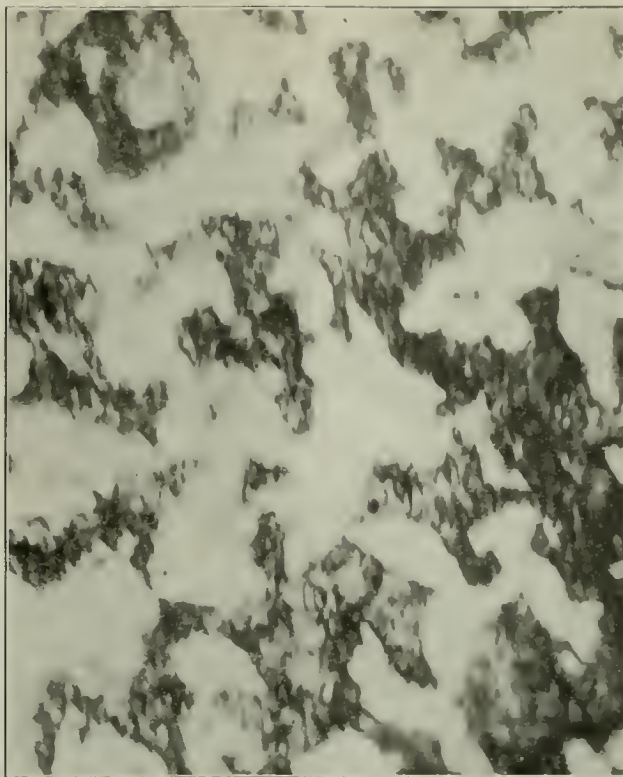


Fig. 3. .40 Carbon Steel x 1000 dia.

lost—merely elongated. Both prints are at 200 diameters.

Fig. 6 is of a .10 per cent carbon steel, rather high in sulphur and phosphorus, magnified 200 times. The arrangement of the pearlite as enlargements of the division lines between the ferrite units is characteristic. The structure developed much more quickly than in

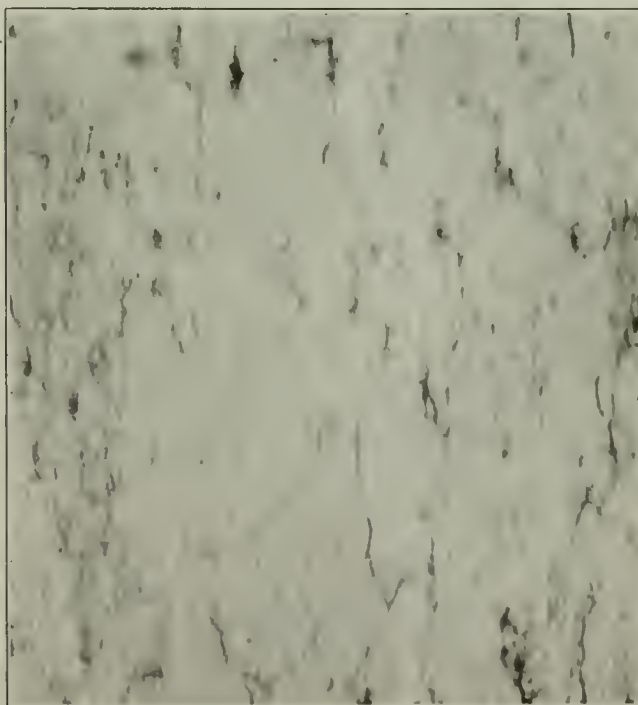


Fig. 4. Electrolytic Iron, Strained.

the case of the pure iron. The grain size is conspicuously small and uniform.

Fig. 7 shows a nut-bar steel, very high in sulphur, at a thousand diameters. This print shows not only the strong division lines between the ferrite cells and the massing of the pearlite in the inter-cellular spaces but the highly granular nature of the ferrite itself. Just why such material should have superior punching qualities might be rather difficult to define from its appearance. Carbon is about .15 per cent in the specimen, although the strong etching and high relief makes the pearlite appear large in proportion to the ferrite.

Fig. 8 is a print from a structural beam of only .12 per cent carbon, badly laminated. The magnification is 350 diameters. The ferrite has its usual cellular divisions.

Fig. 9 is of a .24 per cent carbon forging at 1,000

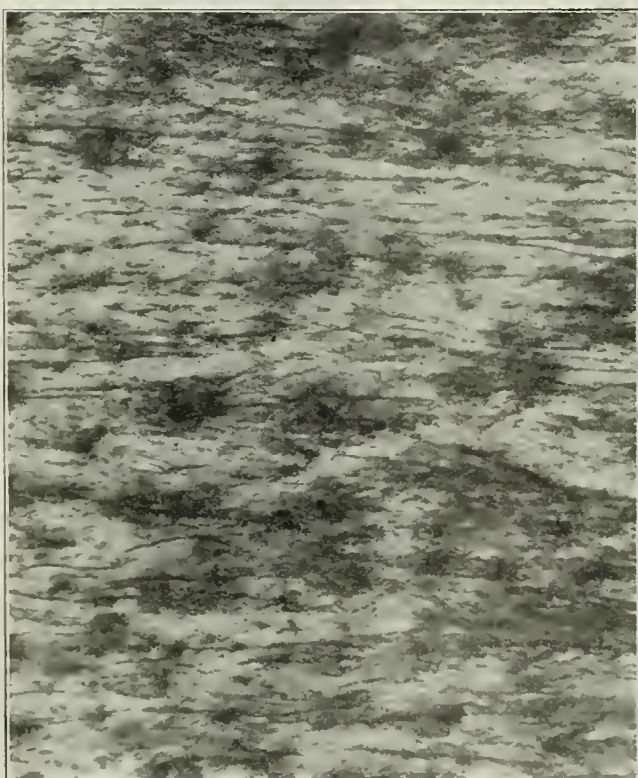


Fig. 5. Electrolytic Iron, at Rupture.

diameters; at small magnifications the ferrite appears as rather angular flakes of slightly granular nature; the higher powers resolve the flakes into units separated by lines and show the real granulations in the ferrite.

This cellular nature of the ferrite has long been known in the purer materials and in those containing little carbon. In examining steels the ferrite masses are frequently observed and spoken of as the "grains" or ultimate units of the constituents. We have seen no case in which these ferrite particles, if large enough to be considered separately as independent from pearlite, cannot be resolved into further units as illustrated. These, then, are the units of grain size quite as important as the size of the structural units. Many things are being discovered about the properties of material

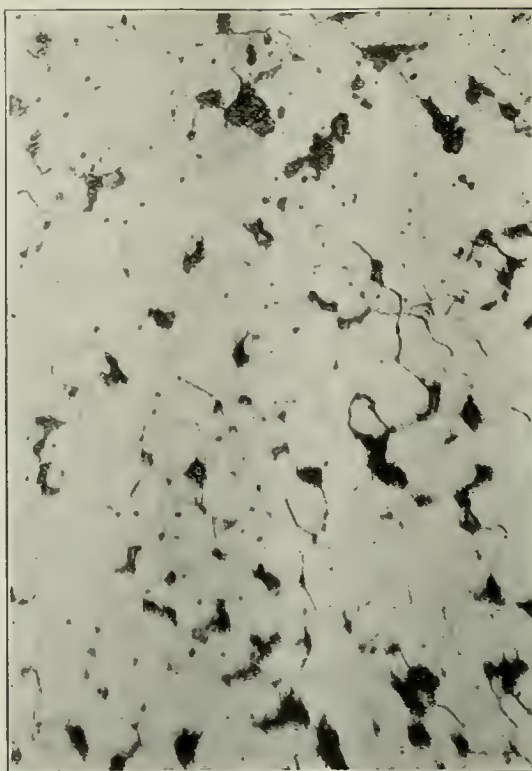


Fig. 6. .10% Carbon Steel x 200 dia.

depending on such grain size, as well as its regulation; topics which cannot be discussed here.

STRUCTURAL GRAIN IN STEELS.

There are three types of grain character which may be recognized in steels. The first we may designate as componental grain; it is the differentiation into

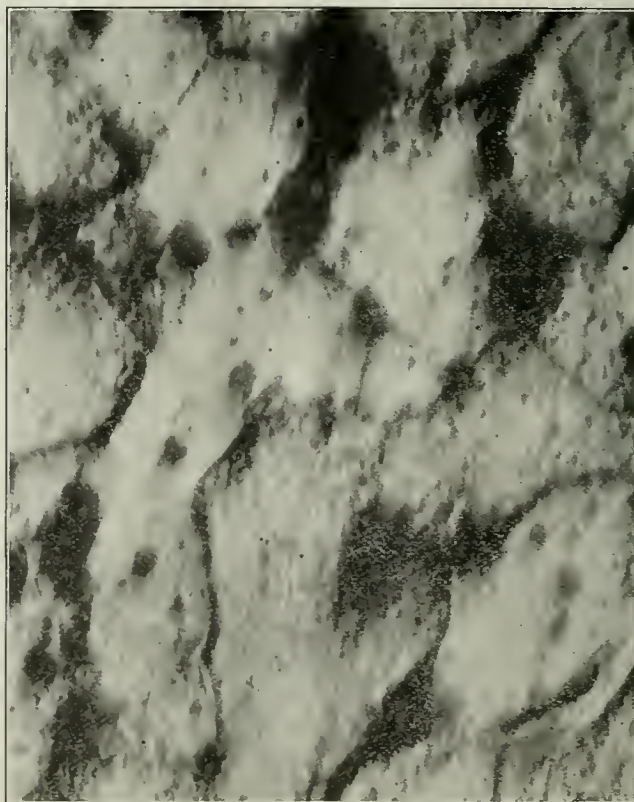


Fig. 7. .15% Carbon Steel x 1000 dia.

units as determined by the components present. Fig. 3 illustrates the case nicely; we have aggregates of ferrite in a ground mass or matrix of pearlite. The ferrite units, as seen, ought most unquestionably to be considered as establishing a grain structure in the material. To clearly define this grain from the two kinds

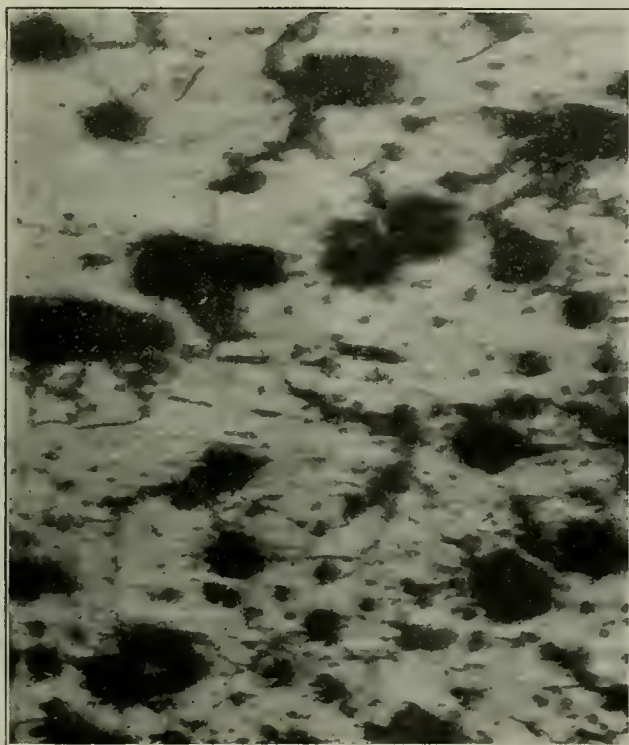


Fig. 8. .12% Carbon Steel x 350 dia.

which will now be mentioned let it be called "componental grain."

The second sort of grain has just been discussed under the heading of the cellular nature of ferrite. It is the sort of unit divisions discernible in homogeneous components; it is a sort of cellular way in which components are internally separated or the individual crystals of the same substance packed together. This grain is easily developed in pure iron and the low carbon steels: wherever ferrite is present in massive formation. This sort of grain is probably not difficult to establish in massive austenite and in massive martensite; the author has seen but one print which indicated that such grain might be found in massive pearlite.

The third sort of grain in steel we may call structural grain. It is a separation of the gross material into units by the particular arrangement, or massing, of one or more of the structural components of the steel in question. Whenever one or more components so distribute themselves that the material assumes definite unit structure from such arrangement this type of granularity is established. Ferrite and cementite are two components chronically prone to build such grain.

Fig. 10 shows a steel with the ferrite thus arranged. The magnification is 100 diameters. Quite likely the dark spots are segregations of impurities; in which case the ferrite and impurities have combined to establish

this enormous grain. Over development of this sort of grain is apt to make steel worthless. It is brought to excess by overheating, by long annealing, by slow cooling without mechanical working, by too much sulphur, by too much phosphorus, and in various other ways. To reduce and keep at a minimum this grain, since it is apparently always injurious, the steel is kept within strict chemical specifications while the mechanical and heat treatment must not violate good practice. The specimen from which Fig. 10 was taken was above standard specifications in phosphorus; the great size of the ferrite inclosures indicates lack of mechanical reduction while hot and cooling—further corroborated by the local development of spots of lamellar pearlite.

Fig. 11 again shows a similar structure, but this time built up out of particles of cementite conspicuously arranged in polygonal form. This specimen shows little evidence of the presence of impurities; its chemical composition is good; the grain is moreover not large enough to cause undue weakness. In fact to a very considerable extent the grain is clearly demolished and confused as should be the case in properly worked tool steels such as this. Carbon in this specimen is just over 1 per cent; magnification 100 diameters.

Structural grain often develops by simple relief pol-

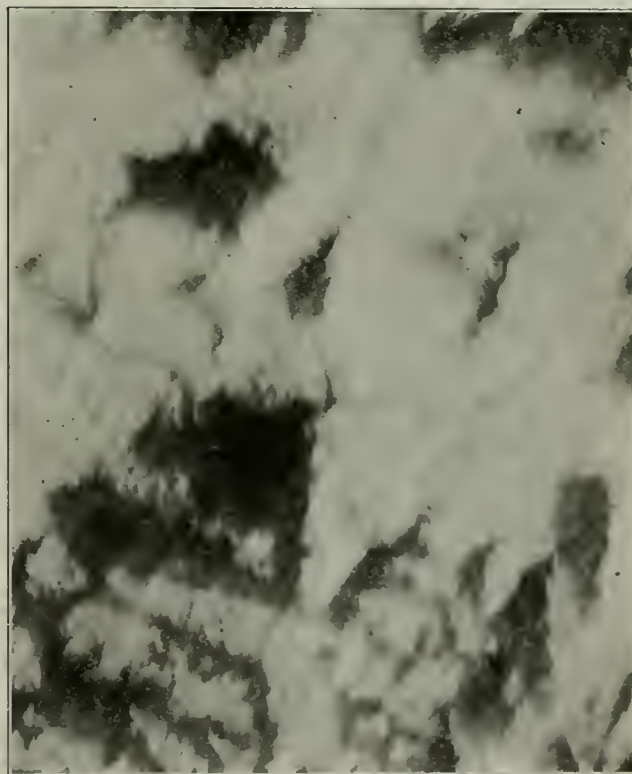


Fig. 9. .24% Carbon Steel x 1000 dia.

ishing; when due to ferrite or cementite it displays itself by etching with picric or nitric acids. We consider it the easiest grain to make visible; it may be so large as to be seen with the naked eye. It is necessarily absent whenever the material contains one component, be that ferrite (pure iron), pearlite (eutectoid ratio, .75 per cent carbon), sorbite or martensite. In steels

of hypo-eutectoid carbon it is built up with extraordinary ease by the massing of ferrite; in hyper-eutectoid apparently with the same facility by the withdrawal of cementite. In steels composed of troostite, osmondite

GRAINLESS STEEL.

The study of steels leads one to consider coarse grain as the direct cause of inferior quality in the metal. We might, then, question if it is possible and



Fig. 10. .55% Carbon Steel x 200 dia.

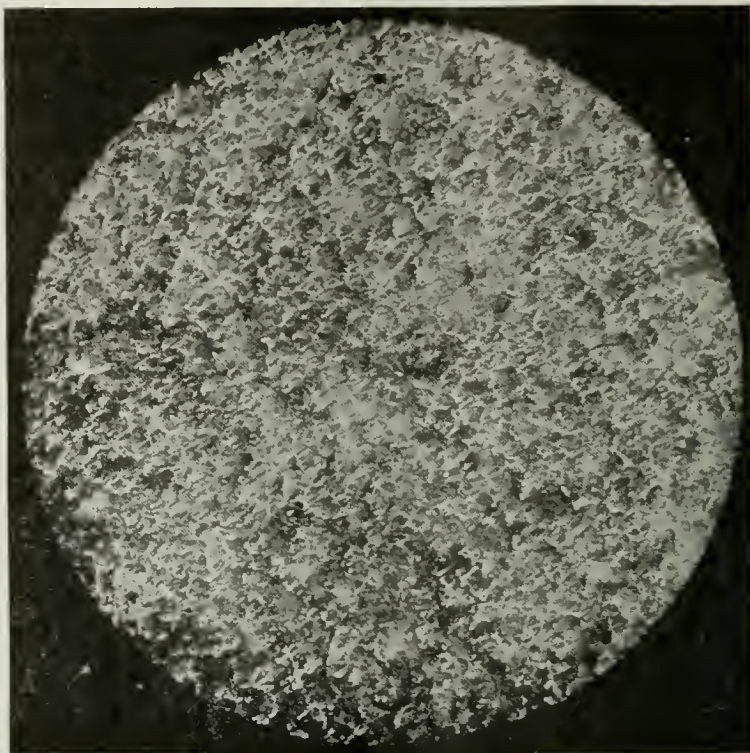


Fig. 11. 1.01% Carbon Steel x 100 dia.

and sorbite structural grain is obviously largely subordinated; the conditions which develop structural grain destroy such components. If troostite develop on the cellular grain boundaries of martensite it is rather

what the result would be of obtaining metal without discernible differentiation of structure. We do not know that this has ever been accomplished; but, we do know that many of the most superior products have

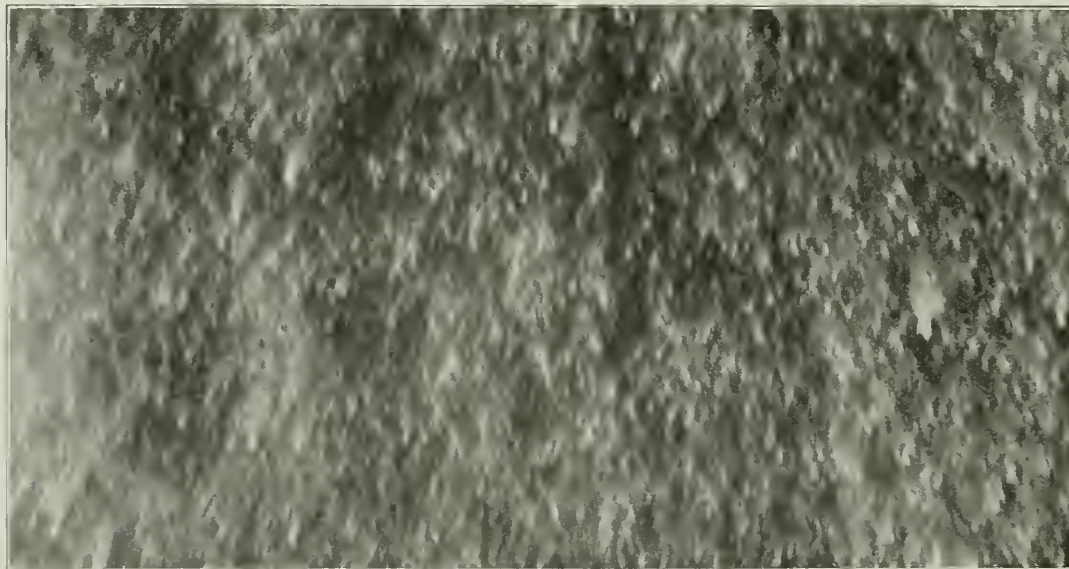


Fig. 12. High Speed Steel x 500 dia.

evidence of such grain than a display of structural grain; for whenever it is attempted to further develop such grain the component is decomposed and more stable aggregates or real metalals (free ferrite, free cementite) are formed.

extremely fine grain, that in the best materials structural grain is absent, that the condition which gives the most desirable combination of good qualities (as in tempered steels) is uniquely that between the solid solution and the separation of visible components with

the carbon in the colloidal state. As the etching or staining of steel in the condition of osmondite or sorbite is difficult of control we can sometimes see these irresolvable masses locally uniform but as to whether or not a cellular grain may be present or not does not admit of proof. Etching to bring out such cellular structure corrodes so extensively that the whole surface is ruined. Further than this, we do not remember any positive assertions or direct evidence of material wholly irresolvable and yet containing neither residues of the still unchanged solid solution nor patches of assembling aggregates.

High speed steels may show the very finest structure and entire absence of cellular or structural grain, yet the componental grain is strongly in evidence. Fig. 12 is a high speed steel magnified 500 diameters; it has been soaked in picric and nitric acids without any effect, sulphur dioxide brought out what structure is to be seen. Further corrosion gives no satisfaction.

Steel without grain is accordingly not to be considered at the present stage of our research; we make material without discernible cellular or structural units but to entirely subordinate metal or aggregate is for the future to accomplish.

SUMMARY.

A shock-proof microscope frame is described and illustrated.

The cellular nature of ferrite is discussed and illustrated.

Structural grain is briefly mentioned, defined and shown.

Note is made of the fact that steel free from at least one of the three sorts of grain detectable is not known at present.

The total quantity of manufactured fuel in the form of briquets, eggettes, coalettes, boulets, and like products, according to E. W. Parker, of the United States Geological Survey, in an advance chapter of Mineral Resources, 1913, on "Fuel Briquetting," just published, amounted in 1913 to 181,859 short tons, valued at \$1,007,327, a decrease of 18,205 tons in quantity but an increase of \$55,066 in value, compared to the output in 1912. The slackened demand for briquetted fuel is believed to be due to the exceptional mildness of the winter of 1912-13 and of November and December, 1913. The briquets which appear to meet with favor in the eastern states are of the boulet type, pillow or egg shaped, and about the size of anthracite nut. They are practically smokeless and make an ideal fuel for the open grate or kitchen range, holding their shape until entirely consumed and then falling, when stirred, into a pulverulent, clinkerless ash. In the Central and Pacific coast states the popular type of briquetted fuel appears to be of larger size, about that of egg coal.

THE PYROMETER IN THE ASSAY MUFFLE.¹

By FREDERICK P. DEWEY.²

Standing alone, by itself, a pyrometer reading has absolutely no value as a control of assay operations in a muffle or as a guide to the assayer in carrying on such operations. The reasons for this are varied and complex. (1) The temperature that controls the success of the operation is that of the lead button undergoing oxidation. At present we have no means of learning this temperature under practical working conditions, so that some suitable place must be selected within the muffle for the location of a pyrometer. (2) Unfortunately, however, there is absolutely no approach even to a fixed relation between the pyrometer reading at any given point available and the temperature of the oxidizing button. The oxidation of the lead supplies much heat to the button, but its effect upon the pyrometer is negligible. One factor governing the amount of heat utilized by the button is the rate of oxidation of the lead, and this in turn is, within wide limits, largely influenced by the passage of the air over the button, so that to fully utilize and apply the pyrometer reading we must also know the height of the barometer and the effect of variations in the barometer readings upon the draft of the particular muffle under consideration. Further and most important, from a practical standpoint, is the freedom of entrance for the air to the muffle. In other words, by manipulating the door or the stopper of the muffle, widely varying differences between the button temperature and the pyrometer reading may be produced. The effect of the door conditions is twofold. It affects the supply of air to the button and also the actual temperature of the bottoms of the muffle on account of the varying amounts of air that have to be heated there in passing through the furnace. Finally the relation of the position of the button within the muffle to that of the pyrometer is vital. Therefore, to intelligently utilize any stated pyrometer reading it is essential to have exact information upon a variety of other conditions surrounding the operation.

Bradford³ pointed out the inconsistencies of various statements regarding pyrometer readings in assaying and well established facts, such for instance as advising a temperature of 700° to 750° for cupellation when it requires at least 906° to fuse litharge. In a series of tests he demonstrated the large amount of heat supplied by the oxidation of the lead and the higher temperature thereby attained by the button. His arrangement of apparatus was ingenious, but risky to the pyrometer couple and not applicable to routine work. He gives an excellent description of the conditions immediately surrounding a cupellation.

¹Presented at the 49th meeting of the A. C. S., Cincinnati, April 7-10, 1914, and published by permission of the Director of the Mint. Published simultaneously by the American Institute of Mining Engineers.

²Assayer, Bureau of the Mint.

³Journal of Industrial and Engineering Chemistry.

Fulton, Anderson, Goodner and Ossa⁴ determined the difference in temperature between an empty cupel and the cupelling lead in an adjoining cupel as 145°, and also give various other temperature determinations, under the conditions employed by them.

For a long time I have been engaged upon an investigation into the conditions surrounding the assay of gold bullion as affecting the accuracy of the results obtained. Naturally the question of the temperature of cupellation early attracted attention, but there were so many other conditions to be investigated where our information was meagre, while the temperature question seemed to be under fairly good control by the eye of experienced cupellers, that the use of the pyrometer was not actively taken up until recently.

In the early days of the investigation various points regarding temperature were carefully considered and some of the problems were worked out. Some of the problems presented themselves with emphasis. In this connection a careful distinction should be drawn between the problem of ascertaining the effect of the various conditions of the cupellation upon the temperature of the cupelling bead and the problem of the regulation and adjustment of these conditions so as to produce the best possible conditions for cupelling, and the final problem of establishing a suitable indicator or guide to show that the proper conditions are being maintained, and especially an indicator which may be applied in different muffles and under varying conditions.

In a broad and general way the time required to work off a given weight of lead is a crude indication of the temperature of the cupellation. When carrying on uniform work in quantity the decreasing size of the button is a general guide for the temperature and a rough notation of the time will often be useful in explaining irregularities of the results. If the general conditions remain uniform, a prolonged cupellation indicates lack of heat, and a rapid one an excess of heat. In making time observations it is essential to adopt some fixed point in the operations to begin taking the time and another to stop. If all the other conditions could be rigidly controlled and the time be very carefully observed, it would furnish a good guide to the temperature, but it would be available only at the finish of the run and could not be used to change conditions during the run. Also, it could not be applied at other times or places or under different conditions. Again it furnishes no preliminary evidence that the furnace is in good condition before starting the work.

It is, however, hardly ever possible to control the other conditions and sometimes accidental variations creep in. On one occasion, when the conditions, including the temperature, appeared to be normal, it became evident that the lead was not oxidizing fast enough. An examination showed that in setting a new muffle the workman had not put the slit in the back of the

muffle exactly opposite the chimney outlet. This choked off the draft and retarded the oxidation. The retardation of the work was, of course, excessive, but this experience emphasizes the natural effect of changes in the barometer upon cupellation. A resetting of the muffle corrected the difficulty.

Another *post facto* temperature indicator is the amount of gold absorbed by the cupel in gold bullion assaying, high absorption under similar conditions, indicating high temperature. Here again controlling the other conditions is difficult and I have found this indicator to be of value largely in emphasizing the fact that variations in the other conditions may falsify the pyrometer reading. It makes a difference whether the pyrometer is rising or falling. If we could hold the pyrometer at the same point for a long time before making the cupellation this cause of difference would be minimized, but this is impracticable in every-day work. It makes a difference if the muffle be new and in good condition or old and nearly worn out, and it must not be forgotten that a new muffle may be poor and leak more than an old one, which was of good quality when new.

The only feasible place to put a pyrometer in an assay muffle is close to the top of the arch of the muffle and for convenience it must be inserted from the back. We all know, of course, that closing the muffle increases the temperature and that on moving toward the back of the muffle the temperature rises, as practical every-day working facts. In order to get a more exact idea as to the difference in the temperature in different parts of the muffle and the relations between these temperatures and the fixed pyrometer readings, a second portable pyrometer was placed on the bottom of the muffle in varying relations to the fixed pyrometer as follows: directly under the fixed pyrometer, at the right side and at the left side in the same cross section as the fixed pyrometer, close to the front in the middle and on each side of the muffle. In some of the arrangements empty cupels were placed beside the bottom pyrometer.

There are three principal causes for differences in the two pyrometer readings: position within the muffle, freedom of entrance of air to the muffle, and condition of the burners on either side of the muffle. In general, the door conditions, governing the entrance of air to the furnace, exert a powerful influence upon the temperature within the muffle, and often cause wide differences in temperature in different parts of the muffle. Under the conditions of these tests, on opening the closed muffle, either pyrometer may fall 100° or more in ten minutes, and a further 10° or 20° before becoming steady. In the closed muffle the two pyrometers registered alike in only one instance, and differed 40° in one. In every instance the movable pyrometer, on the bottom of the muffle, fell more than the fixed pyrometer, at the top of the arch, on opening the closed muffle, and in one instance 40° more.

⁴West. Chem. Met., 4, 31.

A point of grave concern is the stability of the pyrometer. In the above tests both of the pyrometers were practically new and may be depended upon, but the effect of long use, for continuous periods, in the litharge-laden atmosphere of the muffle upon the instrument is unknown. It is known that the hot litharge fume is destructive to the tube, and it is only a question of time when it will affect the enclosed couple. At present there are no ready means for testing the accuracy of the pyrometer from time to time, and it is difficult for an assayer to judge when it is beginning to fail.

In conclusion, I would say that, notwithstanding the objections I have described, the pyrometer occupies a useful field as a general guide to the heat conditions in the assay muffle. In the old and established practice of assaying in the Mint service, in the large laboratories, one or two men do practically all of the cupelling and they grow to be every expert in judging the heat of the muffle and the condition of the cupelling bead by the eye, but the careful and proper use of a pyrometer would often help them, while the man who cupels only intermittently will find it a good general aid. But too much dependence must not be placed upon the pyrometer, and the man who depends upon it entirely will never be a good cupeller.

DISCOVERY OF BARITE IN SOUTHEASTERN ALASKA.

An interesting deposit of barite, or "heavy spar," was discovered by Ernest F. Burchard, of the Geological Survey, while searching for marble deposits in southeastern Alaska in September, 1913. This barite is situated on one of the Castle Islands, in Duncan Canal, a long, narrow bay 3 to 10 miles west of the well-known Wrangell Narrows, and is, by navigable waterways, about 40 miles northwest of the town of Wrangell. There is little in the appearance of the deposit to suggest that it is other than a cliff of weather-beaten, fractured limestone, and it is probable that fishermen have sailed past it or have anchored their boats in its lee for more than a generation, never suspecting that it is composed almost wholly of barium sulphate, a mineral that is very useful but is much less common than those that make up the bulk of rock masses. At any rate, there was no evidence that the deposit had ever been prospected prior to the visit of the survey party. The material must be handled to be appreciated. It is a little softer than limestone but about $1\frac{2}{3}$ times as heavy.

The rock mass formed by the barite stands as a block connected with one of the islands by a low, narrow neck, about 300 feet long, that is covered by water to a depth of 5 to 10 feet at high tide. The top of this barite outlier stands about 35 feet above high-tide level, and the mass is possibly at the maximum 75 feet wide and 200 feet long. According to a rough calculation based on measurements by pacing, there

should be more than 60,000 short tons of barite available above high-tide level. Neither the appearance of the mass nor its geologic relations and structure offer very clear suggestions as to its nature or origin, but it is supposed to represent the residual portion of a large vein of barite, extending parallel to the schistosity of the rock in the adjacent island, which is composed mainly of schist.

The barite, where fresh, is for the most part a finely crystalline, grayish-white rock with thin grayish-blue veins and thin black streaks. A little of the barite is coarsely crystalline and white in color, and some white quartz is present in thin seams and small segregations. Pyrite is nearly everywhere disseminated in fine specks throughout the mass. The thin black streaks are segregations of dark minerals, among which are galena, sphalerite, magnetite, and graphite. On weathered surfaces the material is stained with iron rust resulting from the oxidation of the iron pyrites. The powdered barite is grayish white in color and under a lens shows many particles of metallic sulphides.

Assays show percentages of precious metals too low to classify the barite as a metalliferous ore, and therefore its commercial value will depend on the quality and marketability of the barite itself.

A chemical analysis by W. C. Wheeler, of the Survey, showed the following percentages:

Silica (SiO_2)	5.05
Iron oxide (Fe_2O_3)	.77
Titanium oxide (TiO_2)	None
Calcium oxide (CaO)	Trace
Magnesium oxide (MgO)	Trace
Barium oxide (BaO)	58.60
Strontium oxide (SrO)	.37
Sulphur trioxide (SO_3)	33.69
Carbon dioxide (CO_2)	None
Lead sulphide (PbS)	.16
Zinc sulphide (ZnS)	1.68
Manganese dioxide (MnO_2)	Trace

The material contains about 89.16 per cent of barium sulphate, or barite, and is therefore nearly 90 per cent pure. The chief impurity is silica, which grinds white and is not especially deleterious. The remaining minerals, mainly metallic oxides and sulphides, aggregate less than 45 per cent, although only about 2.98 per cent is shown. These are not high percentages of objectionable impurity and probably are below those carried by shipments of raw barite from many mines.

The barite is not of the highest grade, particularly for use as pigment, and a milling test will be required to determine whether or not it may be possible commercially to remove the metallic sulphides and to bleach the color to a pure white. Simple laboratory tests show that washing and flotation tend to whiten the finely ground grayish-white powder. Further treatment with hot dilute sulphuric acid containing small quantities of sodium chloride and sodium nitrate bleaches the powder nearly as white as precipitated barium sulphate or zinc oxide.

These experiments are encouraging and suggest

that with proper mechanical manipulation the process might be made commercially successful. In the manufacture of lithopone and salts of barium, where crude barite is fused with coal, a slightly impure raw material would apparently react as well as a purer one, providing the impurities were not themselves objectionable. It is possible, therefore, that the Alaska barite is suitable also for general chemical purposes.

To build and operate a barite mill close by the deposit probably would not be practicable, but the raw material can certainly be quarried and loaded on barges very cheaply and transported to Puget Sound or to San Francisco at low freight rates. The approaches to the Castle Islands show, according to Coast and Geodetic Survey charts, from 5 to more than 30 fathoms of water. There is plenty of timber at hand suitable for wharves and the island of which the barite deposit is an outlier contains level space sufficient for a quarry camp.

According to J. M. Hill, of the Survey, the production of crude barite in the United States in 1913 was 45,298 short tons, valued at \$3.45 a ton. The imports of crude barite entered for consumption amounted to 35,840 short tons, valued at \$1.71 a ton. Of these imports 82 short tons were entered at San Francisco, the only Pacific coast port which received any barite during 1913.

PRODUCTION OF PYRITE AND SULPHURIC ACID IN 1913.

The production of pyrite in the United States in 1913, according to W. C. Phalen of the United States Geological Survey, was 341,338 long tons, valued at \$1,286,084. For 1912 the output amounted to 350,928 long tons, valued at \$1,334,259, a decrease for 1913 in quantity of 9,590 long tons and in value of \$48,175. The production in the leading states—Virginia and New York—diminished slightly; in California there was an increased production, and in Wisconsin the output also continued to increase. The output of by-product pyrite, obtained in connection with coal mining, fell off materially.

The imports of pyrite for consumption during the calendar year 1913 were 850,592 long tons, valued at \$3,611,137. These figures show a notable decrease in quantity, 120,193 long tons, and in value \$230,546, as

compared with the imports in 1912, which amounted to 970,785 long tons, valued at \$3,841,683.

According to actual returns for the year 1913 the production of sulphuric acid in the United States was 3,538,980 short tons of 50° acid, valued at \$22,366,482. This output does not include a small amount of fuming acid, but does include by-product acid—that is, acid obtained in the smelter industry. The acid produced at copper and zinc smelters in 1913 amounted to 790,296 short tons of 50° acid, valued at \$4,346,272. The production of acid by grades is given in Table 1:

TABLE I.—PRODUCTION OF SULPHURIC ACID IN THE UNITED STATES IN 1913, BY GRADES, IN SHORT TONS.

Grade.	Quantity.	Value.	Price per ton.
50° Baumé	1,643,318	\$9,212,917	\$ 5.61
60° Baumé	509,929	3,202,528	6.28
66° Baumé	797,104	9,282,422	11.65
Other grades	63,158	986,659	15.62
Total	3,013,509	\$22,684,526	\$ 7.53
Total reduced to 50° Baumé acid*	3,538,980	\$22,366,482	\$ 6.32

*Exclusive of a small amount of fuming acid.

The year 1913 is the third for which the Survey has collected statistical information on the sulphuric acid industry in the United States. The Survey's figures are not estimates, but are compiled from first-hand information received from the producers themselves and can not exceed actual production.

The above figures are final, so far as the Survey's present information goes, but they are subject to change if necessary when the printed report is issued. The changes, if any are made, will probably be slight.

The lignitic coal reserves of the Bonni field region, Alaska, are estimated by the United States Geological Survey to be nearly 10,000,000,000 tons, which exceeds by nearly 3,000,000,000 tons the estimate made a few years ago, on the information then available, of the total quantity of lignitic coal in the territory. The new estimates, which are very moderate, indicate that the quantity of coal available in the Bonnifield region is greater than that of all the other surveyed fields of the territory.

Chronic iron ore mined in the United States last year totaled 255 tons; American imports in 1913 reached 65,180 tons, against only 37,540 tons in 1911. Rhodesia produced about 60,000 tons in 1913.

TABLE II.—PRODUCTION OF SULPHURIC ACID FROM COPPER AND ZINC SMELTERS IN 1911, 1912 AND 1913, IN SHORT TONS. 60° Baumé Acid.

Source.	1911			1912			1913		
	Quality.	Value.	Price per ton.	Quality.	Value.	Price per ton.	Quality.	Value.	Price per ton.
Copper smelters	207,657	\$1,056,185	\$5.09	b 321,156	b \$1,985,704	b \$6.18	336,019	\$2,205,627	\$6.56
Zinc smelters	230,643	1,677,511	7.27	b 292,917	b 2,255,237	b 7.70	296,218	2,140,645	7.23
Total	438,300	\$2,733,696	\$6.24	b 614,073	b \$4,240,941	b \$6.91	632,237	\$4,346,272	\$6.87
Total acid reduced to 50° Baumé.	547,875			c 764,237			790,296		

a The acid reported to the Survey includes that of strength of 50°, 53°, 60° and 66° Baumé, and a small quantity of electrolyte and oleum. All strengths, with the exception of the electrolyte, have been reduced to both 50° and 60° Baumé, as given in the table.

b Inclusive of a small quantity of electrolyte.

c Exclusive of a small quantity of electrolyte.

ZINC INDUSTRY AND TRADE.

The following consular notes on the world's zinc industry and trade have been prepared from information furnished by the various consuls in reply to inquiries made by interested American concerns.

The world's production of zinc (spelter) in 1913 was the largest yet recorded, according to statistics published by the United States Geological Survey. Table I shows the output for the four years ending with 1913:

Countries.	1910 Short tons.	1911 Short tons.	1912 Short tons.	1913 Short tons.
Australia	560	1,904	2,531	4,105
Austria and Italy. .	14,666	18,602	21,609	23,856
Belgium	190,233	215,050	220,678	217,941
France and Spain. .	65,191	70,791	79,543	78,293
Germany	251,046	276,008	298,794	311,914
Great Britain	69,531	73,806	63,086	65,201
Netherlands	23,121	25,059	26,380	26,813
Norway		7,363	8,959	19,040
Poland	9,514	10,952	9,659	9,520
United States	269,184	286,526	338,806	346,676
Total	893,046	986,061	1,070,045	1,103,359

The imports of zinc into the United States for the five years ending with 1913 are shown in Table II:

Years.	Blocks or pigs		Sheets		Old		Value of manufactures	Total value.
	Tons.	Value.	Tons.	Value.	Tons.	Value.		
1909	9,419	\$ 805,087	117	\$ 13,510	238	\$ 9,999	\$6,488	\$835,084
1910	989	95,410	255	36,741	73	5,685	1,526	139,362
1911	323	38,322	291	55,211	104	8,609	7,981	110,123
1912	10,719	1,239,574	728	102,073	147	13,748	8,489	1,363,884
1913			...		...			722,962

Exports of zinc from the United States for the same period are shown in Table III:

STATUS OF THE ZINC INDUSTRY IN AUSTRALIA.

According to the 1912 Official Yearbook of the Commonwealth of Australia, the production of spelter is practically confined to the Broken Hill district of New South Wales, where zinc blende forms one of the chief constituents in the enormous deposits of sulphide ores.

ing turned to profitable account. During 1911 the various process plants on the field were all in continuous operation, and improvements were effected tending toward simplicity of construction and increased capacity. The 1899 exports of zinc (spelter and concentrates) amounted to 49,879 tons; in 1909 they totaled 373,906 tons, valued at \$5,067,388; and in 1911, 516,378 tons, valued at \$6,885,999, the great bulk of the production being obtained from tailings. The following table shows the production of zinc in New South Wales from 1889 to 1911:

Years.	Spelter and concentrates produced. Tons.	Value.
1889	97	\$ 4,808
1891	219	12,760
1899	49,879	239,466
1907	237,219	2,611,461
1908	276,720	2,924,197
1909	373,906	5,067,388
1910	468,627	6,276,004
1911	516,378	6,885,999

During 1913 zinc dust valued at \$44,806 was exported from Melbourne to the United States.

PRODUCTION OF ZINC IN AUSTRIA-HUNGARY.

Zinc ore in Austria is produced mostly in the

Provinces of Carinthia and Tyrol, though it appears in small amounts in Styria and also in other provinces. In 1912 it was produced in 12 active mines employing 500 workmen and 27 overseers. The total output was 34,674 tons of ore, valued at \$577,451. Of this amount about one-half was devoted to Government uses.

Zinc as such is not mined in Hungary. It occurs in the metal mines in the north and east of the country, and a small quantity is produced annually as a by-

Years.	Zinc ore		Plates, sheets, pigs, or bars.		Zinc dross		Value of manufactures.	Total value.
	Tons.	Value.	Tons.	Value.	Tons.	Value.		
1909	12,455	\$412,300	2,556	\$263,010	7,069	\$477,112	\$ 69,751	\$1,222,173
1910	19,711	649,425	3,990	426,560	4,729	380,950	101,336	1,558,271
1911	18,281	642,884	6,872	810,099	4,246	348,176	134,518	1,935,677
1912	23,349	823,997	6,634	864,292	205	17,985	140,027	1,846,301
1913	15,815	631,991	7,783	955,667	29	1,457	145,984	1,735,099

Gratifying results have been achieved in the work of profitably extracting the zinc contents of the large heaps of accumulated tailings and from the ore raised on the Broken Hill field. The year 1909 witnessed the passing of this problem out of the experimental stage and the practical solution of the difficulty which has confronted the mining companies for many years. At present not only is the zinc being obtained in a marketable form, but the silver and lead contents are be-

product of smelting operations. The production of zinc ore and zinc powder amounted in 1911 to 117 short tons, valued at \$1,619, and in 1912 to 857 tons, valued at \$13,961.

It is stated that in the copper, silver, lead, and iron mines the ore is accompanied by sphalerite, galena, calomine, and smithsonite. Sphalerite is said to occur in large quantities at Rezbanya, Bihar County, Boiczan, Hunyad County, and at various other places. The

zinc deposits are for the most part owned by the Hungarian Government, with the exception of certain ones near Nagyvarad and Temesvar, which are the property of the Roman Catholic clergy.

Zinc mining and smelting have received very little attention in Hungary. The Government now appears to be anxious to utilize its deposits and has, it is reported, prepared plans for a smelter to be erected in Transylvania in the neighborhood of the natural-gas wells. No work has yet been done, as the Government has been unable to devote any funds to the project. It has been intimated that the Hungarian Government would be glad to interest American capital in the exploitation of its zinc deposits.

The imports of zinc and crushed zinc into Hungary in 1912 amounted to 8,119 short tons, valued at \$981,919, and in 1911 to 7,967 tons, valued at \$963,729.

ZINC OXIDE, LITHOPONE, AND WHITE LEAD IN GERMANY.

The 1913 statistical year book for the German Empire states the production of oxide of zinc together with zinc dust, both intended for sale, as follows, in metric tons of 2,204.6 pounds: 1908, 11,600 tons, valued at \$849,184; 1909, 17,400 tons, valued at \$1,201,186; 1910, 19,600 tons, valued at \$1,394,442; 1911, 20,900 tons, valued at \$1,664,096.

The imports and exports of oxide of zinc (zinc white and zinc gray), lithopone (zinc sulphide white), and white lead, gathered from the monthly reports of Germany's foreign trade issued by the Imperial Bureau of Statistics were as follows (Table IV) during the five years from 1908 through 1912, in double centners (220.46 lbs. each):

TABLE IV.

Years.	Oxide of Zinc		Lithopone		White Lead	
	Imports.	Exports.	Imports.	Exports.	Imports.	Exports.
1908 ...	50,843	177,367	20,319	86,354	35,580	137,331
1909 ...	45,198	184,385	24,821	75,631	28,898	105,832
1910 ...	46,116	226,703	33,421	105,592	27,799	135,944
1911 ...	49,774	209,943	27,246	137,421	39,379	149,615
1912 ...	60,318	287,315	33,351	151,170	27,086	127,007

ITALIAN ZINC PRODUCTION.

The production of zinc ores in Italy in 1913 reached a total of 100,000 tons, all of which was shipped from Carloforte, Sardinia, to French and Belgian smelters—one-third to France and two-thirds to Belgium. No smelting is done in Italy. Some zinc ore is mined in Bergamo and is said to be shipped from Genoa to Swansea, Wales.

ZINC AND SILVER LEAD IN RUSSIA.

There are deposits of silver-lead and zinc ores in several parts of the Caucasus but almost the entire production of these ores at the present time is obtained from the mines of the Alagir company near Sadon, in the Vladikavkaz district of the Tersky Province, now leased by the Engineer Duken. The works of this company are the only ones in the Caucasus where silver and zinc are smelted. Sadon is situated on the little-known Ossetine military road leading from Vladikavkaz to Kutais (one of only two roads crossing the entire chain of the Caucasus) and is the center of the mining region. Near it are a number of mines—

Sgid, Dakau, Nokkau, Nuzal, and others. It is about 58 versts (40 miles) from the railroad. The principal mines are situated at the mouth of the Sadon gorge where the Sadon River empties into the Ardon River. The deposits consist of a strong vein in protogine.

The total production of silver-lead and zinc ores in the Caucasus in 1912 is reported by the mining department of the Caucasus to have been 28,495 tons, as compared with 26,060 tons in 1911. Silver, lead, and zinc are not exported.

Zinc mines in the Warsaw consular district exist only in the so-called district of Olkusz, which is situated partly in the Government of Kielce and partly in the Government of Piotrkow. In the latter Government are almost all of the coal mines of the Kingdom of Poland. There are two known mines of zinc, the Boleslaw, Government of Kielce, and the Ulisses at Tlukienko, Government of Piotrkow. The first-named mine employs about 525 laborers and the second about 860 laborers. The ore mined in these two mines is almost exclusively used up by the local plants.

In 1912 the two mines yielded 48,427 tons of carbonate of zinc and 18,768 tons of carbonate of zinc containing some lead. The smelting works, owned mostly by French or other foreign corporations, turned out 23,910 tons of zinc and 726 tons of zinc dust in 1912.

TRADE STATISTICS AND RECENT DEVELOPMENTS IN SPAIN.

From the statistics for 1911, the latest available, it appears that 162,140 long tons of zinc ore, valued at \$1,213,649, were mined in Spain that year. The number of laborers in these mines totaled 2,243, and the machinery used was divided as follows: Three hydraulic machines, developing 93 horsepower; 26 steam engines with 532 horsepower; and 19 electric machines with 861 horsepower. The number of productive mines in the country was 44. The most important production of zinc ore is in the Provinces of Murcia, Santander and Cordoba.

There are only two zinc-smelting works in Spain, the more important of which is located in the Province of Oviedo, and is owned and operated by the Real Compañia Asturiana, a Belgian firm, with head offices in Torrelavega, Province of Santander. The works are equipped with 25 Belgian furnaces and three steam engines, developing 190 horsepower; 366 laborers were employed, and 18,500 long tons of zinc ore were smelted in the works during 1911, producing 1,700 long tons of spelter, valued at \$205,020; 3,429 long tons of laminated zinc, valued at \$438,226; and 1,537 tons of refined zinc, valued at \$221,328.

The other zinc-smelting works in the country is in Penarroya, in the Province of Cordoba, and is of lesser importance. It is equipped with two Belgian furnaces and gives employment to 140 laborers. The amount of ore smelted there was 4,562 long tons, from which 1,204 tons of smelter were extracted. New furnaces of the Benker system are now in course of construction in these works.

The exports of blende and calamine for 1911 were as follows:

Exported to— Blende.	Long tons.	Value.
Germany	19,995	\$179,960
Belgium	50,178	451,599
France	15,663	140,967
Great Britain	8,179	73,614
Netherlands	1,180	10,622
Calamine in Natural State.		
Belgium	10,898	94,163
Germany	6,666	57,594
France	455	3,845
Calced Calamine.		
Belgium	9,348	114,418
France	4,570	55,937
Germany	500	6,120
Total	127,632	\$1,188,839

Zinc in bars and sheets was also exported from Spain during 1911, the total being 2,336 long tons, valued at \$294,370. It was shipped chiefly to France, Great Britain, Argentina, and the Netherlands.

With the exception of the low prices ruling in 1913 the conditions prevailing in the zinc industry are about the same as they have been for years past, little having been accomplished to improve transportation facilities in order to deliver the ore at a reduced price at sea-board. Owing to indifferent prices the exports of this ore greatly declined last year, reaching only about 4,000 tons, as compared with 5,000 tons in 1912, 7,000 tons in 1911, and 6,500 tons in 1910. These statistics are derived from private sources, the customs statistics for 1913 being even lower.

It is not known definitely how many zinc mines are at present worked in this Province, as most of the small mines are of little importance and are worked only sporadically. The zinc ore continues to be transported to the port of Almeria in two-wheeled mule carts and on the backs of burros, sometimes for a distance of 20 or 30 miles. All the zinc ore is shipped to Belgium.

The zinc-mine concessions are controlled chiefly by two Belgian concerns, La Société Métallurgique Austro-Belge, of Corphalie-les-Huy, Belgium, and La Compagnie des Minerais de Liège, Liège, Belgium. The first named is really an international concern owning zinc factories in Belgium, France, Germany and Austria. All the zinc ore they extract here is sent to their Belgian works. For the last 40 years this company has been working a group of mines covering about 150 acres near Dalias, northwest of Almeria. When the wind is favorable, the ore is loaded at Roquetas; otherwise it is brought to Almeria.

There are no records of exports of zinc ore to the United States, although the exports of iron ore to America in 1913 were valued at \$467,854.

The new publications of the Bureau of Mines under List 28, May, 1914, include the following: Bulletin 67: Electric Furnaces for Making Iron and Steel, by D. A. Lyon and R. M. Keeney, 1913, 142 pp., 36 figs. Miners' Circular 14: Gases Found in Coal Mines, by G. A. Burrell, 1913, 21 pp.

LIGNITE FROM THE WILLISTON FIELD OF NORTH DAKOTA.

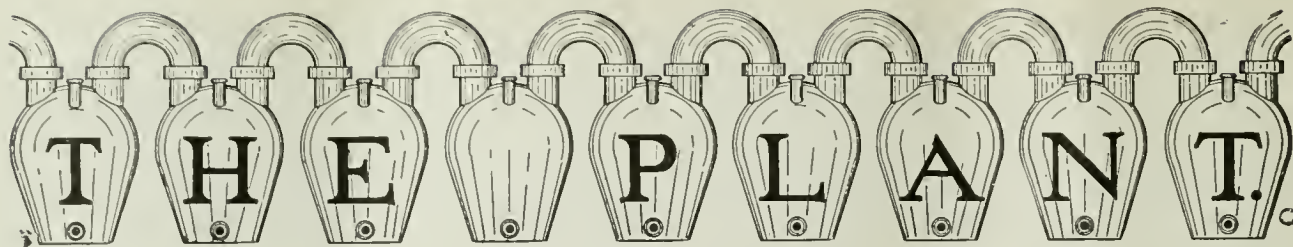
The great deposits of lignite underlying what is known as the Williston lignite field in North Dakota form the subject of a report by Frank A. Herald, recently issued by the United States Geological Survey as Chapter E of Bulletin 531. Several mines are in operation in this field, and one of the plants using the lignite is unique—that of the United States Reclamation Service—in that it burns the lignite at the mines for the generation of electricity that is conveyed over cable lines to Buford, where electrically operated pumps are located. These pumps lift water from Missouri River to the canals of an extensive irrigation system, which waters a large section of the Missouri River valley. The plant, including the mine, is in operation during the irrigation season only, but it furnishes the basis of an important industry. Lignite seems well adapted to this work and can be cheaply mined. It is hauled in pit cars from the mine to a small crusher above bunkers which empty into the engine room. Some of the furnaces are fed by hand, but others are stoked automatically; the fuel is handled well either way.

The Williston lignite is used chiefly, however, as household fuel but also to some extent under stationary boilers. As a domestic fuel it is satisfactory when properly used, but the novice generally meets perplexing difficulties and is likely to underestimate its value. The most satisfactory results are obtained in ordinary cooking or heating stoves when the firebox is well filled with lignite that has been broken into small chunks and dried.

Lignite has been thoroughly tested under power-plant boilers and found to be satisfactory when properly handled. Systematic tests were made at the Reclamation Service power plant in October, 1908, to determine the efficiency of the fuel and to learn the best methods of firing. These tests showed that the lignite is satisfactory for making steam when boilers and fireboxes are properly constructed and the fires are correctly fed and controlled. The result of these tests are set forth in Bulletin 2 of the Bureau of Mines.

Great possibilities exist in the conversion of lignite into producer gas. Though producer-gas plants are numerous in Europe and are becoming common in this country, they are not yet wholly beyond the experimental stage. They have, however, been perfected sufficiently to prove their superiority in many points to ordinary steam boilers.

Some briquetting tests have been made with North Dakota lignite and have proved that the fuel can be treated successfully in that way. Tests at the Pittsburgh laboratory of the Bureau of Mines indicate that lignite from the Williston field can be economically briquetted, and lignite from this field has been briquetted successfully at the North Dakota Mining and Experiment Station at Hebron.



PROBABLE COMMERCIAL APPLICATION OF CHLORINE.

By A. A. Singer, B. S. and Joseph Abelsom, B. S.

The problem of the utilization of chlorine has become very urgent, because the electrolytic soda works produce it in quantities much larger than the demand, and whereas in the past, hydrochloric acid has been used as a source of chlorine, convenient methods for conversion of chlorine into hydrochloric acid are now being sought for.

We will endeavor to show that there is absolutely no need of converting all the chlorine into hydrochloric acid since there are many other fields open for its application.

(1) Recently* an American firm advertised anonymously in the *Metallurgical and Chemical Journal* for a process for the economical production of hydrochloric acid by the combination of hydrogen and chlorine. It is probable that this may be effected in the immediate future by the employment of some such agency as blue or ultra-violet light. While the demand for hydrochloric acid is not near so strong as for sulphuric acid, yet its production from hydrogen and chlorine especially since the development of the production of hydrogen by the electrolysis of water, offers one of the outlets for electrolytic chlorine.

(2) Carbonyl chloride has some considerable application, being used in large quantities in the manufacture of dyestuffs in Germany. Along with the industrial awakening in America, the coal tar industry will be developed. Water gas, which is produced by passing steam over carbon in the state of combustion, is treated with chlorine in the presence of ultra-violet or blue light, or a catalyst (to be determined), carbonyl chloride and hydrochloric acid being produced. Thus it is evident that chlorine, will have a very considerable market in the near future, through the use of carbonyl chloride made by the above process.

(3) In Austria and England, large quantities of industrial solvents as "Westron" and "Westrosol" are produced by the chlorination of acetylene. A similar industry, has never been operated in this country, although there is no logical reason why it should not be initiated. By the chlorination of acetylene, in the presence of catalyst, as antimony pentachloride, or through the agency of photolysis (ultra-violet or blue light), a series of chlorinated derivatives of acetylene may be economically obtained, and all these find many

applications in the industries as detergents and extraction agents.

(4) In Germany, two solvents for resins and gums are on the market, termed "Epichlorhydrin" and "Dichlorhydrin," both of which are produced by the chlorination of glycerine. Inasmuch as the United States ranks as one of the largest glycerine producers in the world, and the demand for varnishes, laquers and other resin solutions is an ever increasing one, the production of such solvents presents an important use of chlorine.

(5) At the recent International Congress of Applied Chemistry in New York (1913), Charles Baskerville presented a paper with H. S. Riederer on the chlorination substitution products from natural gas. The process which is protected by patents and which appeared in the *Journal of the Society of Chemical Industry* in January, 1913, depends on the chlorination of the methane of natural gas (natural gas of Pennsylvania contains from 40 to 95 per cent of methane). In the presence of blue light, we are informed that this process is commercial, and when operated in apparatus of special design, gives an economical yield of hydrochloric acid, chloroform and carbon tetrachloride, or other chlorides of carbon. The methane is chlorinated to the limit, giving hydrochloric acid and carbon tetrachloride. Experimental results have shown that the yields are more satisfactory than in any other process devised for the purpose, and that the other chlorides of carbon as chloroform and dichlormethane may be obtained by reverse substitution; i. e., by the reduction of the carbon tetrachloride with nascent hydrogen. We thus have a process by which means hydrochloric acid, carbon tetrachloride and chloroform may be obtained from a cheap material, natural gas, which in the Pittsburgh district is sold to industrial concerns for ten cents per 1,000 cubic feet.

(6) Another process for the production of carbon tetrachloride is that of A. W. Smith, which is used by the Dow Chemical Co., of Midland, Michigan, and which consists in the chlorination of carbon bisulphide. With the awakening of American manufacturers to the utilization of carbon tetrachloride instead of inflammable benzene or petroleum ether as an extraction material in the fat, rubber and paint industries, it is only to be expected that the demand for carbon tetrachloride will be an ever increasing one. Carbon bisulphide is produced cheaply by the "Taylor Electric Furnace Process" at Penn Yan, New York. By arousing interest among the consumers of extraction agents and sol-

*About June, 1912.

vents, it is likely that another concern having the command of cheap chlorine could exist, and in fact accrue profits in competition with the aforesaid Michigan concern.

(7) By the chlorination of carbon bisulphide under certain conditions, and also by the chlorination of ethane, which may be prepared by several reactions which permit of economical production, hexachlormethane is obtained. This product may also be obtained by the chlorination of natural gas in Baskerville's process. Hexachlormethane even in the crude state, is obtained in the form of asicular crystals, possessing a pronounced camphoraceous odor. The physiological action of this compound has never been studied, but we are informed by one in touch with such matters, that it possesses insecticidal and germicidal properties, and that it may be used instead of camphor for certain purposes.

(8) By chlorinating carbon bisulphide and natural gas, one may obtain, either directly or by reverse substitution of the end product, a compound termed dichlormethane. The solvent properties of this compound have not yet been studied¹ but because of its analogy to the other chlorine substitution products of methane, one must conclude that its solvent action is high.

In much the same manner as we obtain dichlormethane, so can we also prepare monochlormethane, which compound can readily be prepared by the action of hydrogen chloride on methyl alcohol (now selling for \$50 a gallon). On account of the exceedingly low boiling point of monochlormethane, it is surprising that it has never been used or rather applied for refrigerating² purposes.

(9) Owing to the demand for tungsten and vanadium, in the manufacture of tool steels in special ferro-alloys, an economical process for the extraction of these metals from their ores, is always desirable. Chlorine is passed over the heated ore, and the vaporous chloride of the metal is passed into water and hydrolyzes, the hydroxide being formed; hydrochloric acid is also formed at the same time, precaution being observed that the solution always be diluted as regards hydrochloric acid. In the same manner we may extract aluminum from clay.

(10) Fullers earth has been used as an absorbent of bromine in Germany, the product being in stick form (Kieselguhr), and is also used for the sterilization of water. Why not then take wood charcoal which absorbs 200 volumes of chlorine for a deodorizer or disinfectant for water, and in place of formaldehyde for disinfecting sick rooms?³

¹Writers will soon commence work on solvent properties.

²Writers intend to perform research work thereon.

³Now being effected by writers.

CELLULOID: ITS USE IN SHOE FACTORIES.*

CELLULOID BOX TOES AND COUNTERS.

Of late many shoe manufacturers have been using pyroxylin plastic, generally known as celluloid, on an extensive scale. The celluloid is used in the shoes, both in the form of counters and box toes. The use of these counters introduces no great increase of the fire hazard, but the use of celluloid in making box toes increases the ordinary shoe shop hazard materially.

Counters.—In the celluloid counter the celluloid is reinforced on the outside by a small piece of sole leather to give stiffness, and then the whole is covered by a single piece of thin sheepskin covering both sides of the counter, and completely covering and concealing the celluloid. This method of making counters was invented and patented by Mr. G. H. Preble of Lynn, Mass., who sold the manufacturing rights to a Haverhill concern on a royalty basis.

The cost of these counters at present is the same as that of the highest grade of sole leather counters, so that there is no money saved by their use, and their introduction on a large scale in shoe factories is unlikely. Some manufacturers are using them exclusively in all their pumps and oxfords, as they claim that they are entirely proof against the softening effects of perspiration. These celluloid counters come from Haverhill, being brought ready made, and as the celluloid is completely covered by leather they present practically no fire hazard.

Box Toes.—The use of celluloid in box toes is a matter of no small importance. The celluloid is bought in sheets measuring 20x50 inches and 15-1000 inch in thickness, weighing about one pound to the sheet, and comes well crated in strong wooden boxes. The following description covers the conditions found in one factory which probably represents the typical method of using the celluloid. The cutting of tips or boxes from the celluloid sheets is done in the cutting room, where the boxes are cut in lots of 2,000 pairs and tied into bundles of 100 pairs each. The lasters of this factory work in "gangs" of three men each, each "gang" having at its bench a supply of five different sizes of boxes. As there are ten "gangs" and as each hundred pair bundle weighs about a pound and a quarter, it follows that there is 60-65 pounds of celluloid on the laster's benches at one time.

There was also a main supply of celluloid in the lasting room in the form of 100 pair bundles, contained in five half-bushel boxes and which would possibly amount altogether to 100 pounds or more, making the total amount in the lasting room 160-165 pounds.

Before the celluloid boxes are used it is necessary to soften them by immersing in a solvent. Originally

*From the Quarterly Journal of the National Fire Protective Association.

The Minister for Agriculture of New South Wales is advocating government flour mills. The matter is now before the cabinet and mills may be established at wheat centers.

wood alcohol was used for this purpose, but on account of objections made by the men, some factories gave it up and are at present using a mixture consisting of about 70 per cent of denatured alcohol and 30 per cent of acetone, to which is added $\frac{1}{4}$ to $\frac{1}{2}$ per cent of oil of citronella, the latter ingredient being introduced only for the purpose of improving the odor of the mixture. This liquid is used from open tin boxes holding one quart each. The celluloid tips are suspended in this liquid for a few minutes by special hangers, after which they are inserted in the shoe, which is immediately lasted. The lasting is done cold, no heat being used.

It is not possible to use this process on turn shoes, but it is said to be a great success on welt and McKay shoes. It produces a toe easily lasted, which is light, flexible, uniform and perspiration-proof.

The process is said to have been invented by Mr. F. H. Thompson and Mr. F. H. Preble of Lynn, Mass. On account of the opposition of the labor union, the process is not being used in many factories but the inventors expect that it will come into general use as soon as some arrangement can be made with the unions. Celluloid "boxes" are being cut and sold at the present time by the Preble Box Toe Co. of Lynn and shipped to various factories outside of Lynn.

Suggestions.—The introduction of the process should call for the disuse of gas on account of the increased hazard. Electric lights should be installed in its stead. Ventilators are needed to take off the fumes from the alcohol. The boxes containing the solvent should be kept covered when not in use.

The celluloid, both that at the workmen's benches, and the main supply of cut stock, is not usually covered. The supply at the benches should be kept in deep tin boxes with hinged covers, these to be kept closed at all times when not in use. The main supply should be stored outside the factory in strong metal boxes or fireproof vaults, only that quantity necessary for the daily output being brought inside. This latter supply should be kept in tight metal boxes with self-closing covers. Not over 250 pounds of uncut stock should be allowed in main buildings.

These celluloid toe boxes are cheaper than the best grades of sole leather boxes, but are more expensive than the cheaper kinds used in low grades of shoes. From all that can be learned it seems probable that this process will before long be used extensively by makers of high-grade shoes.

CELLULOID-COVERED WOOD HEELS.

The wood heel industry has taken such rapid strides in the last few years that it now plays a most important part in the shoe industry, especially in the manufacture of ladies' shoes.

The principal advantage of the wood heel over the leather heel is that while it is very difficult to fasten the lifts on some shapes of leather heels it is a simple

matter to obtain any shape desired from a block of wood.

Shoe factories using wood heels can be divided into three classes:

(1) Those making the complete heel—this class includes some of the largest factories.

(2) Those buying the wood heel and doing the covering themselves.

(3) Those buying the covered heel already made, as in the smaller factory.

The first class includes factories making the complete heel and covering it.

The wood with which these heels are made is almost always of maple. This wood is bought in planks and sawed into strips wide enough for the desired heel model, the strips being then sawed into pieces about two inches long. These blocks are then shaped on a moulding machine to the desired size and shape. They are treated with a thin solution of lacquer and are then ready for the celluloid coating.

This celluloid, which is a very cheap grade, comes in sheets about 20x50 inches and from 10-1000 to 15-1000 inch thick, a sheet weighing about nine ounces. From four to six of these sheets are fastened together and are cut with dies to the desired shape for covering the heels. Covers for about three pairs can be cut to the square foot. Some concerns cut up a day's supply while others cut them as needed. The covers are sent to the cementing room to be softened and applied.

Softening is done in two ways: first by what is termed the cold process and second by the hot process.

The cold, or immersion process, consists of soaking the cover in a dish containing about a quart of solution made up mostly of wood alcohol with a small amount of acetone. The covers remain from one to six hours in this and they are then plastic enough to stretch around the heel. The heel is held in what is known as a "Jack" which holds the heel on the top and bottom, the cover is stretched around the heel and cemented together at the breast with a heavy amyl acetate lacquer. The "Jack" is then removed and the cover is turned over the top and bottom of the heel, trimmed and cemented at the edges. The heel is now ready for finishing. A bottom lift of leather is fastened to the heel with a screw in the center, and with nails. The heel is then polished on a cloth buffing wheel with "Tripoli" polish, which gives it a smooth surface. The heel is now ready to be fastened to the shoe.

The hot or vapor process consists of softening the cover by means of the vapor given off when a mixture of wood alcohol and acetone is heated slightly. This heating is done in a wooden oven lined with hair felt and metal. The liquid is placed in a pan in the bottom of the oven which is placed over a steam pipe. The covers are placed on a wire shelf above the liquid. The oven is tight except for the cover on top or door on the front for putting in and taking out the covers.

The covers are allowed to remain in the vapor, the temperature of which is between 80 to 100 degrees Fahr. from four to five minutes.

These ovens are about 2 by 2 feet by 1 foot high and one operative has two ovens to attend. The cover or door to these ovens should have springs so as to close automatically and keep the vapor from escaping. From here on the process is the same as in the previous method.

The second class of risks includes those who buy the wood heels and do the coating themselves. In this class the woodworking hazard is eliminated but the celluloid hazard remains.

The third class of risks is those which purchase the wood heels already covered and the hazard is only that due to the presence of the celluloid heels, which is small, as these heels will barely burn.

Hazards.—The woodworking hazard is the same as any woodworker, and a blower system should be connected to each machine to remove the sawdust and shavings to a good, safe shaving bin.

In cutting the celluloid there is a hazard in the celluloid and in the waste from it. Care should be taken to clean up all the scrap celluloid and have it removed from the building as soon as possible. There should not be more than 250 pounds of celluloid in the building at one time. The sheet celluloid and cut covers should be kept in a metal box with a metal cover when not in use and the main supply should be kept outside in a detached shed.

The main supply of liquids used as softeners should be stored outside and that in the dishes and ovens removed every night. The room in which this softening is done should be shut off in a good manner. There should be no open flames in the room, and if artificial light is used it should be incandescent electric with double globe, vaporproof lamps with keyless sockets. The room should also be ventilated to the outside of the building.

Retouching.—In most shoe factories a solution is used to retouch any damage done the uppers while the shoe was being made. Most of these solutions are made up of celluloid in solution with some solvent.

This solution is put on the damaged part with a brush and after drying is buffed or rubbed up.

The retouching solutions come in small bottles holding about half a pint and each operative may have from six to eight of these bottles on his bench.

Practically the only hazard in conducting this work is that of an open flame coming in contact with the gases given off.

Shoe Forms.—Although this class of work will probably not be found in shoe shops it is worthy of mention.

These shoe forms are used for show purposes such as in salesmen samples and in shoes in store windows.

The forms are made of either light wood, fibre-board or pasteboard. The old way was to paint or stain them for a finish and as the call was for a bet-

ter finish, pyroxylin plastic was tried with good success.

There are two ways of coating the form with this. One is to cover the form with the sheet celluloid and the other to apply the coating by means of a spray. The first method, that of applying the sheet celluloid, is similar to that used in coating wood heels. The second, that of applying the coating by means of a spray, is much more hazardous.

In the risk visited the spray is applied as follows: The liquid, which is celluloid and acetone, is purchased in cans and is poured into the sprayer as needed. The container on these sprayers holds about one quart. The air pressure is supplied by an air pump.

The shoe form is held by a wire under a metal hood with a fan which conducts the air and gas to the outside. One coat of this spray is given the form and it is then sanded down and two more coats applied. The finish is obtained by buffing as in wood heels. As the solution comes in any color, any shade can be matched. By this method a coating of celluloid about 10-1000 inch is obtained.

This process should be done in a well cut-off room which is provided with suction fans to carry the vapors to the outside. No open flames should be allowed inside the room and the light should be incandescent electric in double vaporproof globes with keyless sockets. The storage of the solution should be guarded as are other highly inflammable liquids.

A new starch works at Fort Williams, Ontario, which cost in excess of \$1,000,000, has commenced operations. All construction work was done by the Canadian branch of an American company. The machinery mostly came from the United States, the balance from Europe. Many new ideas are carried out in the machinery equipment for saving in cost of producing. Corn will be transformed into starch, glucose, sirup, feed, and by-products, about 3,000 bushels to be ground daily. Pure mountain water is obtained through the Fort William municipal waterworks from Lake Lomond. Shipments of corn are now arriving from Minneapolis, Minn., but an elevator and marine leg for unloading vessels will be erected and the corn brought from Lake ports in the United States. About 175 men will be employed in operating the plant, to which Fort William gave a bonus of \$100,000. It is understood that the eastern Canadian company built this plant in order to supply the trade of western Canada, Fort William being at the Canadian head of the Great Lakes, and from this city three great trunk railways go west.

The construction cost of Norwegian water-power plants varies from \$26.80 to \$53.60 per horsepower for large water plants and from \$26.80 to \$134 per horsepower for small plants. The rate at which the power is sold to consumers varies from \$8.04 for large enterprises up to \$13.40 for small ones, per horsepower per year, 24 hours per day service.

APPLICATIONS OF OZONE.*

By A. VOSMAER.

Ozone is generated by the action of the so-called brush discharge¹ on oxygen, the product being ozone more or less diluted with either non-converted oxygen or air, the later being the rule in actual practice. Though the use of pure oxygen gives a higher concentration of ozone, this increase is not sufficiently high to justify the high cost of the gas. In laboratory apparatus the concentration of ozone can be run up as high as 160 grams per cubic meter, but in regular work on a larger scale it is hardly possible to get more than something like 30 and even that is rather high.

Since the cost per gram of ozone is not a linear function of the concentration, but increases rapidly with concentration, it is fortunate that ozone possesses such wonderful oxidizing powers that concentrations very much lower than those cited are quite sufficient for most purposes. For the manufacture of ozone there are now several ozonators of varying values on the market² and it is necessary to obtain the right kind for the purpose in mind, as it would be wasteful to generate a high concentration ozone and afterwards dilute it with air. Nearly all ordinary work can be done with a concentration of between 3 and 5 grams per cubic meter; a very large amount of work can be satisfactorily carried out with ozone of no more than about one gram, and some special applications require far less yet, down to two-tenths of a milligram, so that there is ample variety.

The only property of ozone that is of commercial importance is its remarkably strong oxidizing power, unless we consider its wonderful power as a germicide to be due to a specific property. I am inclined to do so, but there is evidence also that its germicidal value can be traced to its oxidizing power.

Before discussing the application of ozone in detail, I wish to draw attention to some important points which govern the ozone industry: (1) Ozone is scarcely soluble in water—some say it is absolutely insoluble, which would be very improbable; others claim its solubility to be about ten times that of oxygen which latter statement seems as improbable as the former. (2) Ozone is difficult to make and when made, is difficult to keep; in fact, there is no storage question, the ozone being used when made. (3) As the gas may be considered hardly soluble at all in the ordinary sense of the word, molecular contact between ozone and the substance to be treated fails and one has to make up for it by long and very intimate mechanical contact which in practice means a special apparatus and constitutes the engineering part of the business.

A great advantage when using ozone is that its product of decomposition is a gas which is easily sep-

arated from the material that has undergone the treatment, and with which we are all familiar. It is a matter of diversity of opinion, and open to discussion whether or not ozone when acting splits off one active atom or utilizes all three. In my opinion it is probable that it is all three.

PURIFICATION OF WATER.

Years ago this most important of the possible applications of ozone originated in Holland where non-success in the sterilization of milk lead to successful sterilization of water. The interest of German scientists was soon aroused, and Frohlich of the firm of Siemens & Halske took up the work. Unfortunately, the Hollanders (Tindal and Schneller) ultimately, through lack of pecuniary funds, got on the wrong track and the business failed, not because ozone did not do the work but because Schneller did not know

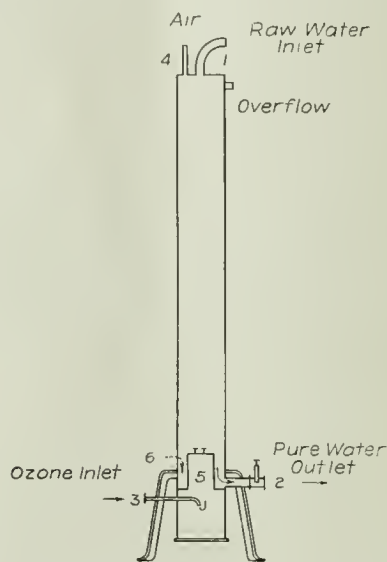


Fig. 1.

how to handle it. To Tindal anyhow belongs the honor of having done pioneer work in this line and later success surely owes much to his attempts.

It takes very little ozone to purify water of ordinary quality, but success depends to a large extent on the apparatus used for the purpose, not only as regards efficiency, but also with reference to purification. It is here that the time factor comes in. To accomplish purification and eventually the complete sterilization of water, it is necessary to have the water in close contact with the ozone, and to keep it so for several minutes. This is the whole secret of the work, but the time factor was generally overlooked in the early attempts.

The ideal apparatus for the treatment of liquors with gases is not at all the well-known scrubber, though this is used to a large extent for that purpose. In the ordinary scrubber, whether made of baffle plates or filled with coke or pebbles, the only method of obtaining a sufficient time of contact between liquid and gas is to make the apparatus so high as to increase the time required by the liquid to reach the bottom when let in at the top, but the upward stream of gas has a speed

*From The Journal of Industrial and Engineering Chemistry.

¹Met. Chem. Eng., 11 (1913), 623 and 705.

²Ibid., 12 (1914), 36.

of its own which cannot be altered; this kind of apparatus does well enough for processes in which absorption is the object, but it has been introduced also in ozone applications and that was a mistake resulting in inefficiency.

The principle of the apparatus I have worked out is shown in Fig. 1. Here the water inlet is at the top and the outlet at the bottom, the reverse being the case for the ozone. By checking the outlet by means of an ordinary valve, the amount of water passing through in a given time can be regulated perfectly up to the maximum; the ozone entering through 3, passes a screen or perforated plate, 5, and then goes upward until it reaches the free outlet at 4. Another perforated screen at 6 serves the purpose of absolutely preventing even the smallest particle of ozone from escaping at the bottom before it has done the work. The height of the standpipe depends upon the quality of the water to be ozonized; if it be a bad water the time of contact has to be longer than with a water of good quality, quality in this particular case referring only to the content of organic matter in solution. Of course, one would expect the height to be greatest in the case of bad water, but that is not the case; on the contrary, there is another way of prolonging the time of contact, viz., by means of increases in diameter. For bad water, evidently, far more ozone is needed than for a good water; this fixes the diameter of the standpipe, because in order to have it work perfectly, it is absolutely necessary that the whole cross area shall be completely filled by a homogeneous mass of gas and water with practically none but surface films of water surrounding the gas bubbles. The downward motion of the water checks the upward motion of the ozone to any desired extent, the natural buoyancy of a bubble being one factor in its movement and the downward force of the water the other. In actual practice this standpipe has to have a height of some 20 or 30 feet and may be made of any suitable material, even iron when properly coated.

There are some interesting details concerning this apparatus: (1) The curious fact that its utter simplicity appeals to nobody unless it is seen in operation. I therefore used to build one of glass so as to show the whole affair outside and inside. Then the fact is evident that as long as there is sufficient pressure in the compartment under the screen 5, there is no chance for any drop of water entering; and the reverse happens at the screen 6 where the water alone passes through. This is easily explained by the assumption that a liquid and a gas cannot simultaneously pass through small openings; at 5 there is excess of gas pressure that causes the gas to take the lead; at 6 there is excess of water pressure which takes advantage of its position, the gas bubbles having no speed at all there. (2) Another thing that used to cause great surprise is that when started for the first time there is one big bubble, say one cubic foot in size, that enters into the water column but after having traveled for about 3 or 4 ft.

it is entirely split up into small bubbles, the ordinary size being about one-quarter of an inch in diameter. This phenomenon, strange as it looks at first sight, is not at all extraordinary. It is entirely analogous to the fact that a vertical stream of water will invariably split up into drops; no matter what the initial size of the stream—the result is individual drops due to the surface tension of the water; in the case of the ozone the same surface tension of the water causes the enclosed gas bubbles to be of a definite size.

The apparatus described is what I would like to call perfection itself. In actual use on a larger scale it can be very conveniently altered so as to be even simpler. Instead of the inlet at the bottom through a perforated screen one can as well have a pipe come down from the top until it reaches the bottom, the whole being then more like the old-fashioned wash bottle of the chemical laboratory. I may add that I have built these sterilizing towers of different sizes, from 6 in. in diameter to 6 ft., and from 10 ft. in height up to 45 ft. In all cases the economical results have been entirely satisfactory. I claim an efficiency of 99 per cent for this apparatus, the average time of contact being four minutes.

As in commercial treatments on a large scale there is necessarily an excess of the reagent, so here it is preferable to have a slight excess of ozone for certainty of results. The excess escapes at the top freely and is too slight to pay for the trouble of recovery. This detail at once proves the advantage of this style of apparatus over the scrubber. I use no more than 1 gram per cubic meter; others use 2.5 grams and as the extra concentration of ozone is not used up in the short time of contact, there is a severe loss if the excess is not recovered. The germicidal power of ozone on water is of such strength that it does not require more than one gram of ozone to treat one million grams (1 cu. m.) of water of medium quality. In a water carrying less than the equivalent of 10 milligrams of permanganate of potash, only about one-tenth this amount of ozone is needed to do the work.

I have never found the slightest difference in the amount of ozone required for purification of water in winter and that needed in summer. A 1-ft. diameter standpipe, the size of the glass one, takes care of up to 30 cubic meters of water per hour, i. e., about 8,000 gals. I have dealt with this apparatus at length because it has given absolute satisfaction in all cases and because it is well adapted for various applications.

The problem of taking iron in solution out of water is one that often presents itself on the other side of the ocean; it can be carried out successfully by the use of air in an apparatus similar to the one just described; as shown by actual practice, the height need not be over 10 or 12 ft. A more difficult problem is to get rid of organic ferric compounds. This can be done in the same apparatus by use of ozone, the precipitated hydroxide of iron being removed by any of the well known methods.

It is quite remarkable that ozone, as a gas, actually burns up most of the organic matter in solution in water and also converts the ferric compounds to ferric hydroxide. As an additional advantage of the use of ozone for the purification of water may be mentioned the fact that any discoloration, odor or abnormal taste is removed so that the result of efficient ozone treatment is a water perfectly clear, pure, colorless and perfect from a bacteriological standpoint. Modern science does not require a water to be perfectly sterile when it has to be used for drinking. It is important to note that the dangerous pathogenic bacteria, more especially the typhoid bacillus and the cholera vibrio, have very little resistance and yield first of all to the action of ozone. What may be left after treatment are such absolutely harmless species as the *b. subtilis* or the *b. mesentericus* and in some cases spores. Fortunately water does not carry any pathogenic spore-forming bacteria.

USE OF OZONE IN THE INDUSTRIAL ARTS.

This subject is not so simple or so well investigated as the former. There have been various trials of ozone in different branches of chemistry, but a good many failed, probably because the experiments were not interpreted in the right way, probably through ignorance of how to apply the new agent, perhaps also in some cases because there was no real opportunity for ozone to supplant the old agent. Certainly the fact that ozone is too expensive has been a reason for non-trial or non-success, but practically the whole field lies open. Aside from some few isolated or unknown instances, ozone has not yet entered the field of chemical industry, but it may do so at any moment.

Its use for bleaching purposes suggests itself first. It has to compete now with that very cheap and efficient agent, chlorine, either as a gas or in the form of hypochlorites of calcium, sodium or magnesium. This competition, solely a question of price per pound, is at present decidedly in favor of chlorine. Whether or not we shall be able to improve our present method of making ozone so as to increase the yield per kilowatt hour is now an open question. The theoretical yield is over a thousand grams and we are getting no more than 10 grams under the most favorable circumstances; hence, there must be a vast improvement before ozone can exceed any other bleaching agent in value. For the present we must accept the cost of ozone as it is—about 20 cents a pound. However, one must bear in mind that it takes two atoms of chlorine to give one atom of oxygen. If my opinion is correct, and the ozone furnishes three active atoms, then 48 grams of ozone gives us 48 grams of O atoms, whereas it takes 70 of chlorine to yield 16 grams of O atoms; this would be an advantage of nearly 5 to 1 for ozone, which would have to be divided by three if we must use 48 grams of ozone to yield only 16 grams of O atoms.

The advantage of chlorine over ozone, however, is evidently not its direct price, but the fact that for the

making of ozone much electrical apparatus is required, whereas chlorine as hypochlorites can be bought in bottles or in barrels. Ozone, however, wins if we do not look solely at direct cost price, but also at quality of product. I have been treating paper pulp with ozone. The result was excellent in so far as concerns the maintenance of fiber, the ozone bleached showing a length of fiber of several times that of the chlorine bleached, but one should be very careful not to use a high ozone concentration, because strong ozone will destroy fiber just as does chlorine; the secret here lies in the proper application of a weak ozone. The bleaching of cotton fabric is even more delicate and the rule must be "Do not hurry." Beeswax is an article that is fairly high priced, and its price is considerably higher when white. The bleaching has been carried out with success but a high concentration of ozone is necessary and a long treatment must be used because there is much organic matter to be removed. The bleaching of sugar molasses solution, on the other hand, is very easy, but the sugar is inverted, which bars this use of ozone. Its use for bleaching glue is also easy, but it deprives the glue of its sticking properties.

More success is to be expected from the use of ozone in the oil industries. Cottonseed oil when ozonized has lost its peculiar taste and smell, but a large amount of ozone must be used to get this result. Sandal wood oil responds more readily to treatment and can be deprived of its taste and bleached also.

The manufacture of white or rather colorless egg-white from blood is not so easy but I have been successful to a certain extent in this line. The bleaching of flour is not at all successful, probably because it has to be done in a dry state. The flour retains a peculiar and disagreeable taste after treatment. The manufacture of varnish from linseed oil is a promising proposition, since the resulting varnish is of remarkable transparency because the oil has not been subjected to any high temperature. It may be that under favorable circumstances the drying of the oil, say for the manufacture of linoleums, may be advantageously done by means of ozone—the advantage in this case being a considerable shortening of time of the process.

The future of ozone is brighter than ever, but we must not exaggerate its importance. If we claimed to be able to sterilize milk or butter by it we would be making false statements. Neither do I believe in its value for aging wines. The flavor of wine is of such a delicate nature and the liability of its alcohol to acidify is so great that one cannot expect any beneficial effect in this line; we all know that even ordinary oxygen will spoil good wine in a couple of hours. What then can be expected of ozone? There are perhaps hundreds of possibilities for ozone, but I do not wish to speak of any with which I have had no personal experience. All my statements come from my own experience and are thus perhaps a bit one-sided,

perhaps too enthusiastic, but that is the inevitable result of 15 years' work.

PURIFICATION OF AIR FOR VENTILATING PURPOSES.

I wish particularly to call attention to the fact that I do not speak here of sterilization of air, but of purification. Dry ozone has no action whatever on dry air with its millions and millions of particles of dry dust. As a means of disinfecting a sick room, ozone, even in strong concentration and moist, is not sensible. Besides bacteria clinging to the particles of dust, there are other sources of contamination. We must consider also volatile products of respiration, perspiration and other gaseous products.

What renders a crowded room disagreeable is not the carbon dioxide of the air, nor lack of sufficient oxygen, but the odor due to the above named pollutions.

Even in a non-ventilated room there is plenty of oxygen for a long time for many people. Each breath takes but a trifling part out of the available total and what makes us feel uncomfortable is not the lack of anything but the excess of bad odors of organic origin. Now ozone is an extraordinarily powerful oxidizing agent and it will take care of these disagreeable odors, harmful not in the direct sense of the word but indirectly because one is liable not to breathe freely and deeply in an atmosphere that has a nasty odor.

Some people think that ozone only masks odors, but it is not very probable that a strong oxidizing agent like ozone would suddenly lose its power, and even if it should, the mere masking would be an advantage.

Dr. Franklin, in order to settle the question of masking vs. oxidation, has been carrying out some very interesting and conclusive experiments to which we can only refer.¹ His conclusions are absolute and convincing in favor of oxidation.

Of course, remembering the extremely powerful action of ozone and thinking also of the delicate character of our mucous membranes, it is an absolute necessity that the concentration of the ozone shall be an exceedingly low one—certainly not over one in a million parts of air and preferably something like one in ten million parts of air when intended for continuous breathing.

The question of purification of air with ozone is two-sided, anyhow: (1) There is the purification of foul air and revivifying it by ozone; (2) there is the question of ozone as a therapeutic agent, e. g., in cases of phthisis in its first stages, anemia, or obesity. I am not competent to give any statements regarding these diseases, but knowing that the inhalation of ozone in a very weak concentration actually does increase the percentage of oxyhæmoglobin in the blood, I believe that this fact, easy to control, should be sufficient to point to the possibility of a beneficial effect.

Even the chance of a possibility of doing something against tuberculosis should be an inducement for medical men to try so simple a treatment as ozone inhalation. As to the other side of the question, one should not lose sight of the influence of psychological conditions on physiological functions. We feel better in a room when there is no smell and to obtain that result we must ventilate to an extent far beyond the necessary replenishment of used up oxygen. What we really use ventilation for is to sweep out odors by large volumes of fresh air and if we can use ozone for that purpose we shall need far less fresh air for replenishment; this in winter means less expensive heating.

The problem of ventilation, however, is not such a simple one, as everybody who has to provide for doing it efficiently knows by experience. Sweeping out the used air has to be done by a large volume of new air which generally means a draft and usually the result is less-efficient ventilation in order to avoid excessive drafts. If we try to express in grams the quantity of organic volatile matter present in a crowded space, we realize its smallness. In fact, it sometimes does not amount to milligrams which explains the fact that ozone, one part in a million, is quite strong enough to take care of the destruction. We need no more than milligrams of ozone to do the work and it is a pity that unloyal objections to its use have been made, for in ozones we have a means of very cheap and efficient ventilation, since a hundred-watt apparatus will take care of the health of a large number of people. We may well remind the reader of the familiar example generally cited in text books on physics to illustrate the sensitiveness of our olfactory nerves. Asafoetida can be detected by its odor when present to the extent of one part in a thousand million million; this is an extreme case, but it is well known that it takes but very little of an odorous gaseous substance to be perceptible. In fact, ozone itself is a good example since one part in ten million of air can be very easily noticed.

As to the amount of ozone required to purify the air in a room, it is safe to say that you should hardly perceive it. If there is a marked odor of ozone it proves that there is too much of it. It would do no harm, but some do not like it from the business man's point of view, it is a wiser policy not to overdose the quantity, and thereby avoid complaints. Some people think ozone will never be used as a therapeutic because all of it is destroyed long before it has reached our lungs. I do not share that opinion for my personal experience goes to show that there actually is an increase in the oxyhæmoglobin percentage and that can be the case only when the ozone is not entirely absorbed by the mucous membranes that it passes on its way to the lungs.

In conclusion I wish to state that the actual applications of ozone are few, but the possible applications

¹"Ozone in Ventilation," Heating and Ventilation, 10, Pt. 1, 30-35, and Pt. 2, 13-18.

are numerous. Ozone can be had now in any quantity and quality and for a price that in many cases is less than that of other oxidizing agents.

LOW SULPHUR CONVERTER STEEL CASTINGS.*

By EDWARD F. CONE.

High sulphur is the *bête noir* of the producer of converter steel castings. Any process that will reduce the sulphur content will command attention. The average commercial product of foundries making steel castings by the use of the side-blow converter contains from 0.060 to 0.095 per cent sulphur. The principal source of this contamination is the coke used in the cupola and, unless there is great care in the selection of both the coke and the raw materials it is not possible to produce a low sulphur metal by the ordinary practice. It can be done, but only at a prohibitive expense.

The production of small steel castings in side-blow converters has increased rapidly in recent years, largely supplanting the same size poured in open-hearth metal. This has been due to the rapid advances in the general quality of the converter metal and to the fact that some plants, devoted solely to the small castings branch of the industry, have been able to give better service in the matter of deliveries. The quality has so greatly improved that the tests now obtained by some of these plants are equaling and even surpassing those obtained by the average open-hearth steel foundry. This is true, even with a high sulphur content.

Just how detrimental sulphur is in steel for steel castings is a debatable point. It is likely that it may cause red shortness, resulting in cracks or checks in the castings which necessitate patching or welding. But even this is doubtful in many cases. Many good sound castings have been and are being made that are high in sulphur. The checking may be due to other causes. Steel foundry men are divided on this question. There may also result an increased amount of manganese sulphide, weakening the crystalline structure. However, this may be some of the buyers of steel castings have come to the conclusion that sulphur above certain limits is objectionable and have adopted specifications to which the producers must live up in order to secure their business. Only recently the Navy

has incorporated a sulphur specification in its requirements, though it had not considered it necessary formerly. Its latest specifications call for an upper limit of 0.05 per cent sulphur. Many of the railroads have the same requirements. It is evident that these steps have developed a situation that renders it extremely difficult for many foundries to obtain some desirable orders.

Spurred on by an incentive not only to overcome this difficulty and improve the metal but also to make a specialty of navy and high grade specification steel castings, a converter foundry in the Chester, Pa., district has developed a process of making low sulphur side-blow steel castings. The Eagan-Rogers Steel & Iron Company, Crum Lynne, Pa., has so modified the regular converter practice that it is able now to hold down the sulphur in its steel to practically any desired limit so as to meet even the most stringent specifications. This has been done by the use of certain slags and also by the method of manipulating the converter. The developers of the process have succeeded in producing and carrying on a basic reaction in an acid converter of the Stoughton type, and thus reducing the sulphur content approximately 40 per cent below that usually obtained in regular practice. Considerable skill and care are required in carrying out the details of the process which naturally are not revealed here. The expected cutting of the lining of the converter is controlled and a dependable practice has been developed.

In addition to this the company claims to have been able, by several new developments in the process, to make its steel nearly constantly uniform and one so close grained that it gives unusual physical results, high in elastic limit and elongation. The table here presented shows some chemical and physical results of special blows by the new process. An average sulphur content of 0.042 per cent is obtained from eight blows. The general uniformity of the carbon, manganese and silicon content is noticeable, equaling steel made by other processes where regulation is easier.

A syndicate has been formed at Nelson, B. C., which will build a factory of 1-ton capacity per day, to demonstrate the possibilities of platinum mining in the Kootenay. Experiments conducted during the past two years have proved sufficiently successful to encourage the building of a \$5,000 plant.

*From The Iron Age.

TABLE OF RESULTS OF SPECIALLY BLOWN CONVERTER STEEL.

Date of blow.	Carbon, per cent.	Phosphorus, per cent.	Manganese, per cent.	Silicon, per cent.	Sulphur, per cent.	Tensile strength, lb. per sq. in.	Elastic limit, lb. per sq. in.	Elongation in 2 ins., per cent.	Reduction of area, per cent.	Cold blend, 1 in. by ½ in., deg.
Feb. 2, 1914.....	0.14	0.036	0.62	0.270	0.047	68,500	47,000	33.0	54.9	180
Dec. 26, 1913.....	0.22	0.050	0.63	0.250	0.045	82,000	58,500	24.5	42.2	180
Dec. 23, 1913.....	0.16	0.050	0.59	0.250	0.047	76,000	45,500	27.5	52.8	180
Dec. 4, 1913.....	0.16	0.046	0.62	0.235	0.032	77,500	49,000	26.5	53.1	180
Nov. 25, 1913.....	0.18	0.043	0.64	0.245	0.034	80,000	55,500	24.0	48.0	180
Oct. 13, 1913.....	0.15	0.046	0.57	0.262	0.048	73,500	53,000	31.0	51.1	180
Sept. 26, 1913.....	0.14	0.039	0.59	0.260	0.030	75,500	51,000	26.0	47.2	180
Aug. 1, 1913.....	0.16	0.048	0.73	0.330	0.050	78,000	50,000	28.5	44.6	180

SAWDUST BRIQUETS IN BRITISH COLUMBIA.

The disposition and profitable utilization of the by-products or refuse from sawmills is a question that is receiving the serious consideration of individuals and companies operating the mills on the Pacific coast. The production of lumber and shingles constitutes one of the principal industries of British Columbia, but on account of the extensive tracts of timberland and the increasing demand for lumber and shingles, it has not yet reached the magnitude to which it promises to attain.

The increasing number of large sawmills, the growing importance of the lumber interests, and the thousands of tons of by-products or refuse in the way of sawdust, splinters, bark, slabs, and small cuttings that are constantly accumulating at the mills, make the utilization of this waste material a matter of importance to the lumber and shingle manufacturers. The following information on this matter is given by Consul General R. E. Mansfield, Vancouver, B. C., in a recent consular report.

The demand for a cheap fuel in convenient form, one that will produce less ash and cinder than coal, has encouraged experiments in the utilization of the by-product of the mills, especially of sawdust in compressed form. Most of the mills now use the sawdust from their plants in the furnaces for the production of steam power, and in some instances for generating electricity.

The conversion of the refuse into fuel possessing greater heat-producing power than the sawdust in its original form promises to develop a profitable industry. It will also lessen the cost of operating the mills by disposing of the by-product that now constitutes an item of considerable expense. The average loss is about 20 per cent of the cut in the manufacture of lumber, and in the Armstrong-Kerr process sufficient residue is obtained from the cutting of 1,000 feet of lumber to make 1 ton of briquets.

The approximate cut of the 220 sawmills, large and small, in British Columbia is 1,350,000,000 feet of lumber annually. The estimated waste from the cut of 1,000 feet of lumber is 350 pounds of sawdust, making a total annual residue from the mills in the Province of 236,250 tons. If this waste material were converted into briquets at a market value of \$6 per ton, the total value would be \$1,417,500.

To meet the demand for the utilization of this waste material, two companies are conducting experiments in the manufacture of briquets. One has a plant in Victoria, that is now turning out a considerable quantity of the new fuel, and the other is constructing a briquet factory in Vancouver for one of the largest lumber companies.

The process employed in the plant at Victoria is described as follows: The bark, slabs, shavings, sawdust, and other portions of the wood refuse from

the sawmills is first passed through a "hog," or edging machine, in which it is cut into pieces not more than three-fourths inch long. The material is then passed into a shredder, where it is reduced to fine particles from the thickness of a match up to a quarter of an inch. From the shredder it passes into a dry kiln, where it is thoroughly dried, as green particles of wood will not adhere and remain in form, no matter how great the pressure may be. From the drier it goes to the heavy compress machine, where it is passed into briquets, or rolls, 3 ins. in diameter, held together with a 7-ply tarred jute string, the only bond used in the briquets.

The cost of production, including depreciation, interest on capital, insurance, etc., is estimated at \$3 per ton. The selling price will be governed by the price of coal, as the new fuel will be a competitor of coal for domestic uses. The manufacturers claim that the briquets as a grate fuel and for cooking purposes, especially for baking, are superior to either wood or coal, as it is more combustible than the latter and leaves less ash and residue than either.

From scientific tests made by experts, the fuel is said to contain 8,614 B. t. u. to the pound, and the ash amounts to 2½ per cent. The company claims that from experiments made recently no ash or residue resulted from the burning of their product, either in a grate, stove, or furnace. It is also claimed that it requires less air to insure good combustion than other fuels, especially coal, and that it does not disintegrate in the process of burning. The plant at Victoria is equipped with three machines with a daily capacity of 7 tons each. The fuel can be manufactured and delivered within a mile of the factory at a cost of \$3 per ton, which is much less than the cheapest grades of Pacific coast coal.

The briquets manufactured by one company are made from sawdust and other by-products of the mills, to which is added tar, pitch, petroleum refuse, or similar substances of an adhesive nature, in sufficient quantities to bind or hold together the principal ingredient. The filler is coal, yellow clay, or other substances, the quantity or proportion depending upon the quality of sawdust used. The cheapest quality of soft coal dust, or slack, including a considerable percentage of dirt and ash may be used to advantage. The composition of the briquets is as follows: Wood refuse, 65 per cent; coal, 25 per cent; pitch, tar, or oil, 10 per cent. The weight is one-third less than that of an equal bulk of coal.

The sawdust produced in the cutting of lumber on the Pacific coast is not really dust but flakes. Cut from softwood with saws especially made for the timber, the residue is soft, spongy, and resilient, and in the raw state is difficult to compress, whereas the sawdust obtainable at the mills in the Eastern States, eastern Canada, and in Europe is from heavier wood, is granular in form, and is more easily compressed, requires less preparation and a smaller proportion of

binding material, and is consequently less expensive to manufacture.

To convert the refuse of the British Columbia mills into briquets, it is necessary first to pass it through a shredder, and then through a pulverizer to reduce it to a consistency from which it can be pressed into proper form.

The machinery required in the manufacture of briquets depends on the material utilized and the preliminary preparation necessary, such as pulverizing, drying, etc. The machines used in one process, designed and built especially for the purpose, are capable of a wide range of adjustment, with a maximum pressure of 10,000 pounds to the square inch. The cost of a compressing machine, with an average capacity of 11,000 briquets per hour, is from \$12,000 to \$14,000. The preparatory machinery consists of special forms of grinders, pulverizers, amalgamators, and mixers. The raw material is measured and weighed automatically, and carried to the various parts of the plant by elevators and conveyors automatically operated.

THE 6TH SEMI-ANNUAL MEETING OF THE AMERICAN INSTITUTE OF CHEMICAL ENGINEERS.

The sixth semi-annual meeting of the American Institute of Chemical Engineers will be held at Troy, N. Y., from June 17 to 20, 1914. The program of the meeting is as follows:

WEDNESDAY, JUNE 17, 1914.

9:30 a. m.—Meeting at Pittsburgh Building, Rensselaer Polytechnic Institute.

Address of Welcome by Honorable C. F. Burns, Mayor of Troy.

Business Session.

Reading of Papers.

The Application of Physical Chemistry to Industrial Processes—W. F. Rittman.

Studies on Filtration—J. W. Bain and A. E. Wigle.

Scrubber for Vacuum Apparatus for Laboratories—Chas. Baskerville.

12:15 p. m.—Complimentary luncheon, Pittsburgh building (courtesy of Rensselaer Polytechnic Institute).

1:30 p. m.—Inspection of the Laboratories of The Rensselaer Polytechnic Institute followed by excursion to U. S. Arsenal. (Manufacture of heavy guns. The shrinking on of the outer jacket of a coast defense gun will be shown if possible.)

5:00 p. m.—Inspection of new Rensselaer Polytechnic Institute Gymnasium followed by swim in the large pool.

7:00 p. m.—Informal dinner at Hotel Rensselaer, followed by reading of papers.

Presidential address—M. C. Whitaker.

The Saratoga Septic Tanks—Wm. P. Mason.

THURSDAY, JUNE 18, 1914.

Excursions.

8:45 a. m.—Excursion to Schenectady to visit plant of General Electric Co. (trolley cars leave from Troy Union depot.)

1:00 p. m.—Complimentary luncheon at the G. E. Works Restaurant (Courtesy of The General Electric Co.)

Alternate Excursions.

2:00 p. m.—Trip to Saratoga; automobile ride to inspect the New York State Reservation, the Springs and the Sewage Disposal Plant.

5:30 p. m.—Return to Troy by train.

2:00 p. m.—Trip to Albany to inspect the slow sand filter beds and mechanical scrubbing filters. (Opportunity will be given to see the process of cleaning the sand beds.)

5:30 p. m.—Return to Troy by trolley.

7:00 p. m.—Subscription dinner at the Troy Club (\$3.00).

FRIDAY, JUNE 19, 1914.

9:30 a. m.—Business Session.

10:30 a. m.—Reading of papers.

Shoddy and Carbonized Waste—L. J. Matos.

Bleaching Cotton Fibre—J. C. Hebden.

Ozone in Ventilation—J. C. Olsen and Wm. H. Ulrich.

The Present Patent Situation—M. Toch.

12:30 p. m.—Luncheon (informal), Hotel Rensselaer.

1:30 p. m.—Excursion to Mechanicsville to visit plant of West Virginia Pulp and Paper Co. (trolley cars start from Troy Union depot).

4:00 p. m.—Excursion to factory of Geo. P. Ide & Co. (manufacturer of collars and shirts).

5:00 p. m.—Return to Troy.

6:00 p. m.—Informal dinner at Hotel Rensselaer, followed by reading of papers.

A Combination Water Softener and Storage Tank, illustrated with lantern slides—L. M. Booth.

Development of Rotary Furnaces, illustrated with lantern slides—R. K. Meade.

Final Business Session.

9:00 p. m.—Smoker at the residence of Wm. P. Mason, 156 First street.

SATURDAY, JUNE 20, 1914.

9:30 a. m.—Visit to Burden Iron Works (Puddling Process for Wrought Iron). Take trolley in front of Rensselaer Hotel.

1:00 p. m.—Luncheon (informal) Hotel Rensselaer.

2:00 p. m.—Visit to Cohoes Filter Plant (Mechanical Filters).

4:00 p. m.—Visit to plant of Freihoffer Baking Co.

HEADQUARTERS AT HOTEL RENSSELAER.

RATES.

Single rooms without bath.....	\$1.50 to \$2.00
Single rooms with bath.....	2.50 to 3.50
Double rooms without bath.....	 to
Double rooms with bath.....	 to



METHODS OF ANALYSIS USED IN THE
LABORATORIES OF THE ARMOUR
INSTITUTE OF TECHNOLOGY.

Permanganate Solutions. (Continued.)

In some determinations involving permanganate solutions, such as the Williams, Ford-Williams and bismuthate methods for manganese, it is necessary to have a solution of ferrous salt of standard strength. This solution should be exactly equivalent in strength to the permanganate solution, matching it volume for volume. This is very readily accomplished, as ferrous ammonium sulphate may be obtained of such high purity as to permit of its being weighed accurately and made up to exactly the required volume with water, and keeps well provided a little sulphuric acid be present. The salt is, indeed, frequently used in weighed portions for the standardization of permanganate solutions. For this purpose it is not, however, recommended as being quite as good as metallic iron or sodium oxalate, for with its six molecules of water of crystallization, it is subject to slight changes in iron content.

In preparing a solution of ferrous ammonium sulphate equivalent to a standard permanganate:

(1) The weight of salt, per liter of solution desired is calculated, weighed accurately and transferred to a breaker.

(2) The salt is dissolved in water containing 25 c.c. of concentrated sulphuric acid per liter, transferred to the measured flask and made up to the mark, care being taken that the whole is at room temperature.

The calculation is as follows:

Assume a permanganate solution of standard 1 c.c. = 0.005 gm. Fe. $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ has a molecular weight of 392, and contains 14.25% iron. 1 c.c. of permanganate solution. $\equiv$ 0.005 gm. Fe, is then equivalent to $0.005 \div 0.1425 \equiv 0.03509$ gm. per c.c., = 35.09 gms. per liter.

Since the factor $100 \div 14.25 = 7.018$, then the iron standard of the permanganate $\times 7.018 \times 1000 =$ wt. of ferrous ammonium sulphate per liter for the equivalent solution.

A solution so prepared should match the permanganate solution exactly, but its relationship to the permanganate should be checked by titration from time to time.

CALCULATION OF THE VALUES OF A STANDARD PERMANGANATE SOLUTION IN TERMS OF VARIOUS SUBSTANCES.

Permanganate solutions are frequently used in the following determinations:

Iron.

Oxalic acid.

Manganese (Williams' method).

Manganese (Volhard's method).

Hydrogen peroxide.

Lime.

Lead dioxide (PbO_2).

Phosphorous in iron ore, iron or steel (Blair's method). It is convenient, therefore, to have on record the values of the laboratory's standard permanganate solution in terms of all of these substances.

Oxalic Acid.—Since $2\text{KMnO}_4 \rightarrow \text{K}_2\text{O} + 2\text{MnO} + 5\text{O}$ in acid solution, and $\text{H}_2\text{C}_2\text{O}_4 + \text{O} \rightarrow \text{H}_2\text{O} + 2\text{CO}_2$, and $2\text{KMnO}_4 \equiv 10 \text{ Fe}$, then $2\text{KMnO}_4 \equiv 5\text{O} \equiv$

450 559

$5\text{H}_2\text{C}_2\text{O}_4 \equiv 10 \text{ Fe}$, and a unit weight of iron is equivalent to $\equiv 450 \div 559 = 0.805$ units of oxalic acid. The oxalic acid standard is therefore the iron standard $\times 0.8051$.

Manganese (Williams' Method).—This method involves the precipitation of manganese as MnO_2 by means of nitric acid and potassium chlorate, the solution of the MnO_2 in a standard ferrous sulphate solution, and the titration of the excess of ferrous sulphate by means of permanganate. It may be used for the determination of manganese in many different bodies, as well as for the determination of the MnO_2 in pyrolusite.

Since $\text{MnO}_2 + 2\text{FeSO}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{MnSO}_4 + \text{H}_2\text{O}$ $1\text{Mn} \equiv 2\text{Fe}$. And as $2\text{KMnO}_4 \equiv 10\text{Fe}$,

559 274.6

then $2\text{KMnO}_4 \equiv 10\text{Fe} \equiv 25\text{Mn}$ and a unit weight of iron is equivalent to $274.6 \div 559 = 0.4912$ units of manganese.

The manganese value of the permanganate is therefore 0.4913 times the iron standard, and the number of c.c. of permanganate equivalent to the sulphate solution used up by the MnO_2 gives, when multiplied by this factor, the weight of manganese in the sample.

When the bismuthate method of precipitation of the manganese is employed, the final solution of the MnO_2 in ferrous sulphate and titration by permanganate is the same as in the Williams method. The same values of the solutions therefore apply to the bismuthate method as to the one just described.

The manganese standard times 1.582F gives the MnO_2 value.

Manganese (Volhard's Method).—This method depends upon the oxidation of divalent manganese as

MnCl₂ or MnSO₄ to the tetravalent condition as MnO₂ in neutral solution, the permanganate being reduced to MnO₂. The reaction is rather complex, giving compounds of varying composition, but the manganese is completely precipitated in the tetravalent condition.

Since $2\text{KMnO}_4 \rightarrow \text{K}_2\text{O} \equiv 2\text{MnO} + 3\text{O}$ in neutral solutions, and $3\text{MnO} + 3\text{O} \rightarrow 3\text{MnO}_2$, then 2KMnO_4

$$\begin{array}{ccc} 559 & 109.9 \\ \hline & \end{array}$$

$\equiv 3\text{O} \equiv 3\text{Mn}$, and as $2\text{KMnO}_4 \equiv 10\text{Fe}$, $10\text{Fe} \equiv 3\text{Mn}$, the unit weight of iron is therefore equivalent to $109.9 \div 559 = 0.2948$, and the manganese standard is equal to the iron standard times 0.2948.

Hydrogen Peroxide reacts with permanganate in the presence of acid according to

$2\text{KMnO}_4 + 5\text{H}_2\text{O}_2 + 4\text{H}_2\text{SO}_4 \rightarrow 2\text{KHSO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O} + 5\text{O}_2$. From this $2\text{KMnO}_4 \equiv 5\text{H}_2\text{O}_2$, and since $2\text{KMnO}_4 \equiv 5\text{O} \equiv 10\text{Fe}$, then

$\begin{array}{ccc} 170 & 559 \\ \hline 5\text{H}_2\text{O}_2 \equiv 10\text{Fe} \end{array}$ and the ratio of hydrogen peroxide to iron is $170 \div 559 = 0.3041$.

The hydrogen peroxide standard of the permanganate solution is therefore the iron standard times 0.3041.

Calcium (or calcium oxide) may be rapidly and conveniently determined by permanganate titration as follows: The calcium is precipitated in the usual manner as CaC₂O₄. The precipitate is freed from ammonium oxalate by washing and then decomposed by hot dilute sulphuric acid with the liberation of oxalic acid. This oxalic acid is then titrated in hot solution according to

$2\text{KMnO}_4 + 5\text{H}_2\text{C}_2\text{O}_4 + 3\text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O} + 10\text{CO}_2$. From this, $2\text{KMnO}_4 \equiv 5\text{H}_2\text{C}_2\text{O}_4$, $5\text{H}_2\text{C}_2\text{O}_4 \equiv 5\text{CaO}$ in calcium oxalate, and

$$\begin{array}{ccc} 559 & 280.4 \\ \hline & \end{array}$$

as $2\text{KMnO}_4 \equiv 10\text{Fe}$, then $10\text{Fe} = 5\text{CaO}$.

The ratio of lime to iron is therefore $280.4 \div 559 = 0.5016$, and the CaO standard of the permanganate solution is the iron value multiplied by 0.5016. The CaO standard times 0.7146 gives the calcium value.

Blair's Method for Phosphorus.—This excellent method depends upon: (1) The precipitation of the phosphorus from the sample of iron, steel, iron ore or other material containing small quantities of the element, according to the usual methods, as $3(\text{NH}_4)_2\text{O} \cdot 5\text{P}_2\text{O}_5 \cdot 24\text{MoO}_3$, ammonium phosphomolybdate.

(2) The solution of this precipitate in ammonia solution, with subsequent acidification by sulphuric acid.

(3) The reduction of the MoO₃ in the precipitate by means of zinc in the presence of sulphuric acid, to Mo₂O₃. (The actual reduction by zinc and sulphuric acid takes the MoO₃ completely to Mo₂O₃. This compound is, however, very susceptible to oxidation by the air, and the formula Mo₂O₃ has been found empirically to represent the composition of the reduced solution in contact with the air in the flask.)

(4) The re-oxidation of the Mo₂O₃ to MoO₃ by titration with a standard permanganate solution.

The chemical changes may be represented as follows:

In (3) $24\text{MoO}_3 + 35\text{Zn} + 35\text{H}_2\text{SO}_4 \rightarrow \text{Mo}_2\text{O}_3 + 35\text{ZnSO}_4 + 35\text{H}_2\text{O}$.

In (4) $\text{Mo}_2\text{O}_3 + 14\text{KMnO}_4 + 21\text{H}_2\text{SO}_4 \rightarrow 24\text{MoO}_3 + 7\text{K}_2\text{SO}_4 + 14\text{MnSO}_4 + 35\text{H}_2\text{O}$.

From these reactions it is seen that $2\text{P} = 24\text{MoO}_3$
 $\begin{array}{ccc} 62 & 3913 \\ \hline \end{array}$
 $= 14\text{KMnO}_4$ and as $2\text{KMnO}_4 = 10\text{Fe}$, $2\text{P} = 70\text{Fe}$, and the ratio of phosphorus to iron is $62 \div 3913 = 0.0158$. The iron value of the permanganate solution multiplied by 0.0158 gives, therefore, the phosphorus value.

PERMANGANATE SOLUTIONS.

Iron value $\times 7.018$ = ferrous ammonium sulphate value.

Iron value $\times 0.8051$ = oxalic acid value.

Iron value $\times 0.4912$ = manganese value (Williams or bismuthate).

Iron value $\times 0.2948$ = manganese (Vollhard).

Iron value $\times 0.3041$ = H₂O₂ value.

Iron value $\times 0.5016$ = CaO value.

Iron value $\times 0.0158$ = phosphorus value (Blair).

MILLING OF WHEAT AND TESTING OF FLOUR.*

By HARRY McCORMACK.

There is one great industry which thus far has depended very little on the service of the chemist and chemical engineer in the preparation and marketing of its products. I refer to the wheat and flour milling industry.

During the year 1912, approximately 400,000,000 bushels of winter wheat valued at \$323,000,000 and 330,000,000 bushels of spring wheat valued at \$231,000,000 were produced in this country. Practically all of this wheat is marketed as such or made into flour and marketed with no particular reference to its chemical composition. No particular attention is paid to the composition of wheat which is used for seed, as the product obtained from it is sold on optical inspection rather than on chemical analysis.

The principal markets for wheat in this country are: Chicago, Minneapolis, Duluth, St. Louis, Milwaukee, Kansas City and Omaha. The rules of the Boards of Trade governing the inspection and grading of wheat received in these markets are not uniform so that a dealer in Minneapolis selling wheat to Chicago parties may have wheat of one grade in Minneapolis and find that it is wheat of another grade when it reaches Chicago. This fact has accounted for much of the difficulty encountered by grain dealers under inspection of Federal officials seeking to enforce the Pure Food laws.

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The grading of wheat on the Chicago market may be taken as typical of the grading at all of the principal markets mentioned, as the differences are not very marked and all of them recognize the same varieties and grades of wheat, viz:

Winter Wheat, Spring Wheat, Pacific Coast Wheat and Mixed Wheat. The Winter Wheat is classified as White Winter Wheat, under which there are four grades depending upon the weight per bushel and the percentage of other varieties of wheat present in the mixture; and the same number of grades of Red Winter Wheat and Hard Winter Wheat, depending upon the same conditions. Under the division of Spring Wheat, we have the sub-divisions: Hard Spring Wheat, Northern Spring Wheat, of which there are four grades: White Spring Wheat with four grades corresponding to those under Spring Wheat, Durum Wheat of which there are four grades and Velvet Chaff Wheat of which there are four grades. The Pacific Coast Wheat is Red or White; each of these have three grades, depending as do the other wheats on the weight per bushel and the percentage of dirt and mixed varieties present with it.

The grading of this wheat, as it comes on the market, is primarily a matter of the exercise of judgment on the part of the buyer and seller. Many times their decision is at variance with that of the grain inspector or his judgment may conflict with that of either the buyer or the seller. In such a case there is no definite recourse for any of the parties concerned. The question can be decided only by the judgment of parties not interested in the transaction, but who have no more definite basis for their opinion than have the first parties concerned.

This condition of affairs has led some of the large millers and also some of the large grain companies to seek the services of the chemist, to see if a more satisfactory basis for trading in wheat cannot be reached. The present paper aims to present some of the problems encountered in the attack on this problem and will attempt to point out some of the conditions which it will be necessary to meet before the handling of wheat on a scientific basis is possible.

Grain dealers primarily interested in the establishment of a scientific basis for buying and selling of wheat are those who really buy and sell wheat, not mere traders on the Board of Trade and, in addition to this, they are the dealers whose trade is largely with the milling interests. The miller, of course, is interested primarily in securing a wheat which will give him a satisfactory flour with as large a yield of the better grades of flour as is possible. By the term satisfactory flour, we mean a flour which corresponds in grade to the customary product of his mills and which meets the demands of his customers. It may be a so-called Hard Winter Wheat flour, a Soft Winter Wheat flour, a Hard Spring Wheat or a Soft Spring Wheat. These names are supposed to refer to the wheat from which the flour is milled, but do not always. We have many

instances in which Winter Wheat flours contain no Winter Wheat and other instances in which Spring Wheat flours contain no Spring Wheat. At the same time these flours must meet in a general way the prevailing demands for color and texture, which are supposed to be characteristic of flours milled from these varieties of wheat.

A person not familiar with the variations in wheat composition may be of the opinion that wheat of the same variety, from the same locality, will not vary much in composition from season to season. This, however, is incorrect as has been shown by the work of Le Clerc and others who have studied the effect of varying climatic conditions on the same variety of wheat. Further than this it has been shown by the same investigators that the same variety of wheat grown in different localities will change very materially in composition. Taken in connection with this, it is necessary to state that a grain dealer in the largest market rarely has accurate information as to the precise origin of the sample of wheat he is purchasing. These statements indicate the necessity for a constant examination of the samples of wheat being purchased.

We must realize, at once, that the laboratory milling of a wheat cannot be done in the same manner as in the mills of the large flour manufacturers. We must then, at the outset, take into account the fact that it is impossible for us to mill experimentally a flour which can be compared directly to the flour produced in the large mill and at this point, it may be well to say that the grading and testing of flour is very largely a matter of comparison. The miller desires a wheat as has been said, which will give him his customary flour. The wheat which will do this is determined by milling it experimentally and comparing the flour produced with the flour he is producing in his mill. This will mean that if the comparison is to give any indication as to the value of the wheat in producing the desired flour, the methods of milling the wheat must be the same at all times for the same variety of wheat. Any variation in the milling will produce a variation in the flour and thus an incorrect opinion as to the value of the wheat may be deduced. This is shown very clearly in Tables I and II, which give the results obtained on the same sample of wheat sent to several laboratories, these being the ones best known to the milling trade and with the highest reputation for the character of their work. These tables show, very clearly, that each laboratory has its own method of milling and to some extent its own method of testing a flour obtained by this milling. The majority of laboratories milling wheat and testing flour have approximately the same laboratory milling equipment, yet the way they conduct the milling differs and leads in most instances to quite different results. Table I shows the comparison of the flours produced, using a soft winter patent as standard. Table II gives the original data from which these comparisons on Table I were computed.

The milling apparatus employed in preparing the flours, the data upon which are presented in this paper, is a standard type of experimental milling equipment and will, therefore, be described at this time.

The milling equipment consists of a special Allis-Chalmers experimental mill comprising three sets of 6-inch rolls and a jib bolting machine. Two sets of the rolls are corrugated: one set 16 and 12 to the inch and the other 24 and 18 to the inch. These rolls grind dull to sharp and the fast roll runs a little more than twice as fast as the slow one. The smooth rolls have

crease. In these experiments a Eureka Horizontal Close Scourer was used. It removes the crease dirt, a considerable portion of the outer bran coat, and the beard from the end of the kernel. The scourer is capable of wide adjustment to suit various sizes of stock, and this particular machine was built to scour as closely as possible and also to deliver all the product at the exit openings of the scourer, leaving no residual material to contaminate the succeeding sample. A sufficient quantity of wheat, usually 1,200 grams, is weighed out for scouring. The loss in scouring is

TABLE I—COMPARATIVE FLOUR TEST REPORTS ON THE SAME WHEAT BY DIFFERENT LABORATORIES TWO SAMPLES OF THE SAME LOT OF KANSAS NO. 2 HD FURNISHED TO EACH. ALL FIGURES REFERRED TO SOFT WINTER PATENT AS 100 PER CENT PERFECT.

	Armour Grain Co.		Lab. C.		Lab. D.		Lab. B	
Gluten, per cent	9.15	9.15	9.5	9.0	9.36	9.68	9.3	9.4
Ash, per cent	0.46	0.47	0.44	0.45	0.483	0.466	0.43	0.43
Absorption, per cent	56.0	56.0	54.7	53.8	54.2	53.3	57.0	57.0
Color	100.0	100.0	100.0	100.0	94.0	93.0	92.0	92.0
Loaves per barrel	102.6	102.6	100.0	99.7	100.0	100.6	100.0	100.0
Size of loaf	106.0	106.6	97.9	101.5	105.2	100.5	100.0	100.0
Quality of loaf	102.0	102.0			100.0	100.0	98.5	98.5
Average value	102.7	102.7			99.7	98.4	97.6	97.6
Ferment period	100.0	100.0			111.0	111.0	101.3	101.8
Quality of gluten	103.0	103.0			115.7	109.8	98.6	98.1
Per cent straight flour milled	65.0	65.5	74.5	75.0	66.49	61.02	67.0	67.5

It will be noted that each laboratory except D milled on the two samples approximately the same amount of flour. The results obtained in testing the flour are fairly concordant, too, where the same amount of flour is milled. Laboratory D, with considerable variation in milling, also shows considerable variation on the values reported for certain tests.

a differential of 7 to 10, that is, the fast roll makes 10 revolutions while the slow one makes 7. Accurate adjustment of the rolls is provided by two large screws on the side of each roll, which allow the rolls to be adjusted so that they are in the same plane, and by two smaller screws to set them parallel. The rolls are thrown "in" and "out" by means of a lever. A mechanical jig bolting machine completes the equipment of the mill. Frames of standard bolting-cloths are made to fit this jig; and as many as four frames may be inserted at one time.

Before going to the mill the wheat must be clean, as that term is ordinarily understood. This is usually accomplished by the use of some sort of fanning mill, which does not, however, remove much dirt from the

determined and 1,000 grams of this cleaned wheat is weighed out for the milling.

Any successful milling of a wheat requires the very gradual reduction of the wheat flour and it is in this gradual reduction that the experimental mill falls short of what may be accomplished with a commercial milling equipment. At the same time, the experimental milling must follow along the same lines as the commercial milling if the flour obtained is to accurately represent the flour-producing value of the wheat.

A somewhat extended line of experiments convinced us that it is necessary to decide for each variety of wheat approximately the quantity of straight flour we desire to produce from it and then mill in such a manner as to produce the very best flour possible from

TABLE II—REPORTS ON MILLING AND BAKING TESTS ON THE SAME WHEAT BY DIFFERENT LABORATORIES. EACH SENT TWO SAMPLES OF

	THE LOT OF KANSAS NO. 2 HD. Armour Grain Co.		Lab. D.		Lab. B.		Lab. C.	
Wheat protein	10.9	10.7	10.6	11.0	11.01	11.33	10.9	10.8
Wheat ash	1.90	1.92	1.70	1.60	1.55	1.575	1.73	1.73
Wheat moisture	12.5	12.7	11.0	10.3	8.68	9.18	12.2	12.2
Milling Test—								
Wt. wheat milled, grams	1000.0	1000.0	2000.0	2000.0	985.0	975.0	800.0	800.0
Passes on rolls	3 Coarse 2 Medium 7 Smooth		Same		6 Coarse	6 Coarse	3 Coarse	Same
					9 Smooth	10 Smooth	12 Smooth	
Wt. of bran, grams	297.0	283.0	78.0	85.0	250.0	250.0	200.0	200.0
Wt. of shorts, grams	53.0	62.0	258.0	258.0	80.0	130.0	65.0	60.0
Wt. of flour, grams	600.0	622.0	1490.0	1502.0	655.0	595.0	535.0	540.0
Flour protein	9.15	9.15	9.5	9.0	9.33	9.57	9.3	9.4
Flour ash	0.46	0.47	0.45	0.44	0.483	0.466	0.43	0.43
Flour moisture	12.48	12.18	12.80	12.50	12.25	12.50	13.2	13.3
Baking Test—								
Absorption	56.0	56.0	54.7	53.8	54.2	53.3	57.0	57.0
Time of max. exp., min.	167.0	179.0	316.0	328.0	151.0	150.0	180.0	180.0
No. of rises	2.0	2.0			4.0	4.0	3.0	3.0
Vol. of loaf, cu. in.	86.1	84.9	186.0	193.0	90.0	86.0	102.2	102.0
Flour per loaf, grams	340.0	340.0	340.0	340.0	340.0	340.0	350.0	350.0
Wt. of loaf, grams	490.0	492.0	489.0	487.0	410.0	416.0	515.0	510.0

the wheat and of the percentage previously determined. Different varieties of wheat are capable of producing different quantities of first-class straight flour and any attempt to produce more than this percentage of flour from these wheats will at once lower the quality of the flour secured.

Our experimental work convinced us that the Northern spring wheats gave the best straight flour when milled to produce about 66 per cent of product. Hard winter wheats produced the best flour when milled to about 63 per cent of straight flour. Soft winter wheats should not be milled to produce an excess of about 58 per cent of straight flour. A more intensive milling of any of these wheats leads at once to a marked reduction in color and also to an increase in the percentage of ash, both showing that bran particles are finding their way into the flour. This is most marked on the soft winter wheats and the result of a too intense milling of a No. 2 red soft winter wheat is shown in Table III.

The adjustment of the rolls in the experimental mill will be determined by the size of the wheat kernels being milled. The wheat should pass through the rolls set first so that the wheat kernels will be cracked and this as lightly as possible. They should then be

TABLE III—MILLING TESTS ON SAMPLE OF NO. 2 RED WHEAT.
Showing the Effect to Too Intense Milling.

Milled to	65.5	58.5	Color	94.0	101.0
Gluten	9.6	9.5	Average value....	95.3	98.5
Ash	0.43	0.37	Qual. of loaf....	96.5	100.5

brought closer and closer together until they finally run almost touching as the wheat receives its final milling on this set of rolls. After each passage through the rolls, the product goes to the sieves. Our customary arrangement of the sieve is to place at the bottom of the jig a No. 11 flour sieve, on top of this a No. 34 bran sieve, and on top of this a No. 16 or No. 18 coarse bran sieve. In the first set of rolls only the product remaining on the upper sieve is remilled. When the milling has been completed on the first set of rolls, which will be accomplished in about three passes on these will be sufficient. The material from both the first and second bran sieves is then weighed up and discarded from further milling operations. Up to this time, only a very small percentage of flour has been produced and has found its way from the flour sieve to the receptacle provided for it. The material remaining on the flour sieve then passes to the smooth rolls for final milling. In our laboratory, it is customary to pass the material through the smooth rolls eight times, with sieving between each passage and with the space between the smooth rolls being made smaller and smaller. Practically all of the flour is produced in this milling on the smooth rolls. The material remaining on the flour sieve after this milling is weighed up and discarded. The material which has passed through the flour sieve is resifted through a

No. 13 flour sieve to remove some of the bran particles and dirt which may have escaped the No. 11 sieve and is weighed to give the percentage of flour produced. The flour produced in this way should be very uniform in texture and color, and should be entirely free from any specks of bran or dirt.

The flour thus produced will compare very favorably with the straight flour produced in any commercial mill. It will, of course, not be equal to the patent flour marketed from a commercial mill, as this patent flour is made by taking the straight flour milled and by subjecting it to a system of air separation and sieving to remove much of the bran particles and some of the germ, which otherwise find their way into the straight flour. The patent flour will vary with different mills and brands all the way from 45 per cent to 90 per cent of the straight flour milled.

The milling description, which has been given, applies to wheats which have recently been harvested and which contain their normal moisture content. In case the wheat has been harvested for some months and has lost a considerable percentage of its normal moisture, it is necessary to add water to the wheat and allow this water to be taken up by the wheat before milling. This process is known as tempering and is for the purpose of softening the bran layers so that they will flatten out in the rolls instead of cutting up.

The methods of milling are stated because they are the ones we found best and not because we believe it is impossible to improve on them. These methods are suggested for use until better ones are devised and until the various laboratories can agree on a common method of milling.

At present each laboratory is a law unto itself in its methods of milling. They are like us, they know their methods are best and have no use for the methods used in any other place. Many of them seem to think the milling of wheat is a secret process and thus instead of disclosing in their reports the methods of milling employed in producing a flour, the testing of which is covered in report, the report is formulated in such a way as to conceal as much of the process as is possible.

This led us to send out some samples of wheat to certain laboratories, these samples being accompanied by a data sheet such as we desired filled out. Most of the laboratories supplied the data requested, but from some of them we were never able to secure statements covering their methods of operation which were complete enough to enable us to make an intelligent comparison between their methods and results and the methods and results as obtained by ourselves and others. The data we were able to secure is shown on Tables IV to VII inclusive.

It is our opinion that most of the variations shown throughout this data sheet are due to variations in milling, as when we sent out flour samples for comparative tests the results were more concordant.

The determinations made in the chemical analysis of the flour are: ash, moisture, total nitrogen, and on some samples gliadin nitrogen.

These determinations were made in the customary way. It is, therefore, unnecessary to describe them further than the following comments:

TABLE IV.—COMPARISON OF REPORTS ON THE SAME LOT OF WHEAT BY DIFFERENT LABORATORIES.

No. 2 Spring Wheat. Milling, Baking and Chemical Data.				
	Armour Grain Co.	Lab. A.	Lab. C.	Lab. B.
Wheat protein	14.3		13.1	13.8
Wheat ash	1.87		1.8	1.88
Wheat moisture	12.1		11.2	12.2
Milling Test—				
Wt. wheat milled, grams.	1000.0		2000.0	800.0
Passes on rolls.....	3 Coarse 2 Medium 7 Smooth			3 Coarse 12 Smooth
Wt. of bran, grams....	297.0		93.0	200.0
Wt. of shorts, grams....	53.0		298.0	65.0
Wt. of flour, grams....	632.0		1487.0	535.0
Flour protein	12.75		12.6	12.3
Flour ash	0.49		0.50	0.45
Flour moisture	11.56		12.7	13.2
Baking Test—				
Absorption	56.0	67.0	56.8	61.0
Time of max. exp., min..	181.0	125.0	310.0	205.0
No. of rises.....	2.0			3.0
Vol. of loaf, cu. in.....	88.2	38.0	203.0	109.0
Flour per loaf, grams....	340.0	100.0	340.0	350.0
Wt. of loaf.....	494.0		494.0	515.0

Ash can best be determined in an electrically heated muffle furnace, first at a low temperature, then increasing to a full red heat.

Moisture can best be determined using a glass tube to contain the sample: a tube about $\frac{1}{2}$ by 3 ins. is used and placed in the oven horizontally. After drying it must be weighed in a telescopic weighing tube as it is highly hygroscopic.

Some trouble was experienced in the distillation for the nitrogen determination when a certain type of safety bulb tube was used. Some of the alkaline liquor was invariably carried over; it is recommended, therefore, that only the form known as the Hopkins safety bulb tube be used.

These determinations are made use of in the valuation of a flour about as follows: The ash tells us in a rough way about how much of the bran has found its way into the straight flour milled, as the patent flours have the lowest ash of any on the market. The patent flours made from the different varieties of wheat have somewhat nearly a constant ash and by comparing the ash of our straight flours with those of the patent flours obtained from corresponding varieties of wheat, we have a measure of the value of a wheat which is being tested for its production of patent flour.

The moisture determination is used in calculating all of the samples tested to a constant basis of moisture content. It is also used in calculating the quantity of water absorbed by the flour in the preparation of a dough of standard consistency.

The nitrogen determination is on the same basis as the ash determination. It is a comparison between

the nitrogen of the straight flour and that of the patent flour prepared from the same varieties of wheat. As the nitrogen on the whole wheat is higher than in either the straight flour or the patent flour prepared from it, the value of the wheat as a source of patent flour varies inversely as the ratio between nitrogen in straight flour and nitrogen in patent flour.

The determination of gliadin nitrogen is made in order to compute the ratio between total nitrogen and gliadin nitrogen. In general, the higher this ratio the higher is the quantity of the flour. Whole wheat flours have the lowest gliadin number and there is a constantly increasing ratio from the whole wheat up to the patent flour. Some determination of total nitrogen, gliadin nitrogen and the gliadin numbers are shown in Table VIII.

TABLE V.—COMPARISON OF REPORTS ON THE SAME LOT OF WHEAT BY DIFFERENT LABORATORIES.

No. 2 Red Wheat. Milling, Baking and Chemical Data.				
	Armour Grain Co.	Lab. A.	Lab. D.	Lab. B.
Wheat protein	11.5		11.33	11.30
Wheat ash	1.93		1.55	1.82
Wheat moisture	10.7		8.45	11.8
Milling Test—				
Wt. wheat milled, grams	1000.0		975.0	800.0
Passes on rolls.....	3 Coarse 2 Medium 6 Smooth		6 Coarse 10 Smooth	3 Coarse 11 Smooth
Wt. of bran, grams....	303.0		290.0	195.0
Wt. of shorts, grams....	47.0		80.0	70.0
Wt. of flour, grams....	606.0		605.0	535.0
Flour protein	9.58		9.41	9.6
Flour ash	0.47		0.45	0.39
Flour moisture	11.32		12.25	12.65
Baking Test—				
Absorption	54.5	62.0	51.6	57.0
Time of max. exp., min.	174.0	113.0	14.0	150.0
No. of rises.....	1.0		4.0	3.0
Vol. of loaf, cu. in.....	78.5	34.5	96.0	102.2
Flour per loaf, grams..	340.0	100.0	340.0	350.0
Wt. of loaf.....	492.0		415.0	510.0

TABLE VI.—COMPARISON OF REPORTS ON THE SAME LOT OF WHEAT BY DIFFERENT LABORATORIES.

No. 2 Spring Wheat. Spring Patent as Standard.				
	Armour Grain Co.	Lab. A.	Lab. C.	Lab. B.
Gluten, per cent	12.75		12.6	12.3
Ash, per cent	0.45		0.50	0.45
Absorption, per cent ...	56.0	67.0	56.8	61.0
Color	100.0	87.0	98.0	98.0
Loaves per bbl.....	95.0	101.8	101.0	99.4
Size of loaf	100.0		100.0	100.0
Quality of loaf.....	100.0	90.0		98.5
Average value	98.7			97.7
Fermenting period	100.0			103.6
Quality of gluten.....	100.0			96.6
Per cent straight flour milled	65.0		74.3	67.0

TABLE VII.—COMPARISON OF REPORTS ON THE SAME LOT OF WHEAT BY DIFFERENT LABORATORIES.

No. 2 Red Wheat.				
	Armour Grain Co.	Lab. A.	Lab. D.	Lab. B.
Gluten, per cent.....	9.58		9.68	9.60
Ash, per cent	0.47		0.45	0.39
Absorption, per cent...	54.5	62.0	51.6	57.0
Color	102.0	95.0	95.5	94.0
Loaves per barrel.....	100.0	98.3	99.6	100.0
Size of loaf.....	99.0	90.7	112.4	100.0
Quality of loaf.....	101.2	97.0	100.0	99.0
Average value	100.5	95.4	101.6	98.2
Fermenting period	100.0	132.8	111.0	102.7
Quality of gluten.....	98.5	89.3	109.8	97.4
Per cent straight flour milled	65.0	45.0	62.05	67.0

The testing of the flour for its bread-producing qualities is carried out in all of the laboratories in about the same way and, as previously stated, there is not much difficulty in getting concordant results from different laboratories working on the same sample of flour.

The determinations made in the baking test are absorption, color, the size of the loaf, the texture of the loaf and fermenting period, and from these determinations are calculated the loaves per barrel, the average value of the flour and the quality of the gluten. The absorption is expressed as the quantity of water necessary to add to a hundred parts of flour to make a dough of standard stiffness. The other figures are comparative using the standard flour as 100 per cent on each of the items mentioned.

There are two general types of dough-handling adapted to the baking of tinned bread. These are generally known as the "sponge" method and the "straight dough" method.

In the sponge method somewhat less than one-half of the flour is mixed with an equal weight of water and all other ingredients. It is then allowed to ferment for $1\frac{1}{2}$ to 2 hours, depending on the type of flour, and is then mixed with the remainder of the flour and water to make a dough of the proper consistency. It is then allowed to rise twice and is formed into loaves, placed in the pan in which it is to be baked, and allowed to rise a definite amount. It is then baked. The complete operation takes about $4\frac{1}{2}$ hours.

TABLE VIII.—PROTEIN AND GLIADIN DETERMINATIONS WITH CALCULATED GLIADIN NUMBERS.

Description of wheat from which flour is made.	Protein.	Gliadin.	Gliadin No.
No. 1 Hard Spring—			
1102	11.2	6.62	59.1
1108	11.3	6.70	59.3
No. 1 Velvet Chaff—			
1103	11.4	6.97	61.1
1109	11.6	6.90	59.5
No. 1 Blue Stem—			
1104	11.8	6.92	58.6
1111	11.9	6.92	58.1
Duluth No. 1 North—			
1105	11.3	6.92	61.2
1107	11.7	6.87	59.7
No. 1 Hard Spring—			
1106	11.6	6.95	60.0
1110	11.8	7.07	60.0
Spring Pat. (purchased)	10.8	7.40	68.5

The straight dough method is in general the same as the sponge method with the omission of the sponging stage. In other words, the dough is mixed to the proper consistency for baking at the very start of operations instead of after a sponging stage. This naturally subtracts the time of sponging from the operation and enables a far larger number of samples to be handled.

In fact, with the same equipment, it has been found that just double the number of samples can be handled in one 8-hour day if the straight dough method is used instead of the sponge method. The quality of the loaves will be uniformly slightly lower, but the

results being comparative with each other, this cannot affect the test.

For the above very potent reasons, the straight dough method is used in our laboratory.

THE BAKING TEST.

Method.—A modification of the baking tests as outlined in Bulletin 117 of the Kansas State Agricultural College was used, because several things were thought necessary to bring the test into such form that its results would more closely give the actual commercial value of the flour.

For instance, it as found that some flours from the red wheats of the southern states could not be baked satisfactorily by the above original method, whereas they are used to good results in practice. The modification that follows gives very good loaves.

In making baking tests on different flours it is, above all, desirable that the test should be so conducted that the differences in the results should be caused by the inherent qualities of the flour and not by variations due to the method employed. However, in practice the skilled baker adapts his method to suit the different flours he uses, and he remedies the defects in the flour to some extent by the method of baking he uses. Therefore it has been the writer's aim to conduct these tests in such a way as to get as good bread as possible from the different flours, and if necessary to vary the method of baking in some slight details to be able to do this. That such a method will yield results that more closely approximate the results the flour is going to give in actual use is apparent.

The actual baking and its associated tests were made as follows:

The Straight Dough Test.—In these tests "dough" means a flour mixture that has been subjected to a short period of fermentation and baked as soon as the dough has risen a standard amount. This amount is fixed by preliminary trial and is uniform in all these tests. The short period of fermentation varies from 1 to 3 hours and is secured by using fresh yeast in large quantities.

Before making the dough we must know the percentage of water that the flour will absorb to be of correct stiffness. This is found by weighing out 30 grams of the flour into a strong teacup and running in distilled water from a burette until the resultant dough is "right." The best test that the dough is "right" is to put it on the bottom of the cup in the form of a round ball and watch it for about three minutes. If it gradually settles down until it touches the rim of the circle on the bottom of the cup it is satisfactory. If it stays in the original shape it is too stiff, whereas if it quickly subsides and overlaps the edge of the cup it is too thin. This test will be found to be sensitive in careful hands to within $\frac{1}{4}$ c.c. on 30 grams of flour. The water that the flour absorbs is figured in percentage.

Now the dough can be made: 340 grams of flour, 10 grams of sugar, and 5 grams of salt are weighed

out. The amount of water as determined by the absorption test, less 50 c.c., is also measured out. The flour is placed in the pan in which it is to be baked and placed in the constant temperature oven until it reaches 35° C. As many grams of yeast as are necessary for the whole batch of loaves are weighed out and dissolved in enough cold water to just be able to draw out 50 c.c. of the resultant solution for each batch of dough: 10 grams of yeast should in this way get into each batch of dough.

When the flour is warmed to the right temperature it is removed from the oven and two-thirds of it is placed in a dish. The water as measured out is heated to 42° C. and the sugar and salt dissolved in it. Then exactly 50 c.c. of the yeast solution are withdrawn in a pipette and added to the sugar and salt solution. The temperature of the resulting mixture should be very close to 35° C. This liquid mixture is then added to the flour. The resultant batter is beaten up with a large spoon or spatula until there are no more lumps, which usually takes about two minutes. The remainder of the flour is then added and the dough mixed, first by means of spatulas and then the hands, to a ball of well-kneaded consistency. After this operation, which usually takes but two or three minutes, the dough is placed back in its pan, which has been buttered in the meantime, and put back in the rising oven where it is kept at 35° C. The dough is weighed at this time to ascertain the loss during the kneading. This loss is unavoidable, and usually is about 15 grams. It is due mostly to evaporation of moisture and sticking of some dough to the hands.

The dough is now allowed to rise the standard amount and if it is a very weak flour from a soft wheat, it is immediately baked, but if the flour has any reasonable strength it is knocked down, re-kneaded, and allowed to rise a second time, and at the termination of this rise if the dough of one of the loaves shows signs of collapsing that loaf is then baked, otherwise a third rise is used. Most flours coming from sound wheats will stand three rises; they will even need them. The times of rising are carefully noted, and all loaves are baked exactly 30 minutes at 238° C. About one-half to three-quarters of an hour after the loaf has been standing in the open air, it is weighed, and this weight is recorded as the weight of the hot loaf. This must, of course, be corrected for the small amount of dough lost in the kneading.

In measuring the volume of the loaf it is put in an oblong box that already contains some turnip seed. Then the box is filled with the seed, gently rapped, and the seed leveled off at the top. The seed is poured out and weighed, and from the weight of seed that the box will contain when there is nothing but seed in it, the volume of the loaf can be obtained, since the volume of the box is known. This method has been found to be accurate to within 5 grams of seed, which correspond to about 2-5 cu. in. in volume.

The volume should be measured approximately one hour after removing the loaf from the oven as it will shrink more and more the longer it stands.

GLUTEN EXPANSION DOUGH TEST.

This is for the purpose of testing the quality of the gluten and checking the relative fermentation period of the flour. The procedure is identical with that for the straight dough except that 100 grams of flour are used instead of 340 grams, and the other ingredients in proportionate amounts. At the point where the regular dough would be panned, this dough is placed in the bottom of a well greased glass cylinder which is at a temperature of 35° C. and placed in the rising oven at 35° C.

For the first hour no attention is required, but after that the height of the dough and the time should be recorded every 15 minutes; and later when it is evident that the dough is near its maximum volume, every five minutes. When the dough just begins to fall the volume and time are noted. From the difference in initial and final volumes the relative qualities of the glutes are calculated. Since we start with the same amount of flour, the quality of the gluten itself will be equal to the net rise divided by the per cent gluten in the sample. This figure is then referred to the similar figure of the standard flour on a percentage basis.

Another method of performing this test which seems to yield more definite results uses the gluten itself instead of the dough. For this purpose the gluten is washed out of the flour in the usual way, and then 10 grams of each gluten are placed, wet, in a tin cylinder 1 inch in diameter and placed in the bake oven at 200° C. It will be found that the gluten will expand and after twenty-five minutes will have formed a porous column within the tin. The height of this column will be directly proportional to the quality of the gluten.

In making all these tests, there is selected and tested at the same time a flour the baking qualities of which are known. The results are compared on a percentage basis and in this way the unknown flour is judged.

We are led from our laboratory experience to make the suggestion that some form of mechanical kneading apparatus which can be kept at constant temperature should be used in all of the kneading operations. If this is not done, there is considerable chance for variation in the results obtained for fermenting period, texture and size of loaf. We also suggest that the color be determined on the samples of flour rather than on the bread and that this color be determined with an instrument such as the Lovibond tintometer and that it be expressed in the number of standard color used rather than by any percentage system which may be based on the standard flour. At present there seems to be a different method of expressing color in use by each laboratory engaged in flour testing.

We may sum up the results we have been able to obtain in our experimental work on the milling of

wheat and testing of flour by saying that we are able to secure results which are satisfactory to us in showing the flour-producing qualities of any wheat. We shall qualify this statement by saying that, at the present time, it is very difficult to express our results in such a way that they will convey an adequate understanding of these results to other parties such as millers or flour jobbers.

The primary object of this paper is to present the need for uniform methods to be employed in the milling and testing operations and a uniform method of expressing the results obtained so that any party receiving a report from any laboratory on any particular wheat or flour, will be able to read this report intelligently and to compare it with any other report which he may receive from this or any other laboratory on the same sample of wheat. It is impossible to interest the millers, or to any considerable extent the grain dealers, in the testing of wheat and flour, until they are able to obtain concordant and satisfactory reports on any sample which they may submit.

The first move in the satisfactory solution of this question must be made by the chemist and the chemical laboratories who are seeking the trade of the grain dealer and the miller. The importance of this work may be inferred to some extent by stating that on single days in the past year one firm of grain dealers disposed of, to millers, more than 200,000 bushels of wheat.

Another factor which enters into the importance of such work is that in many years the wheat crops of certain localities are short, while an abundance of wheat of a different variety may be obtainable from other sections. This is very well illustrated by the conditions of the past year, when the winter wheat crop throughout the country was unusually low. Millers using quantities of winter wheat in their milling mixture had to pay a considerable premium above the normal price of wheat to secure varieties of wheat they desired. In some instances this premium amounted to 16 cents per bushel or \$160 per car. Substitutes for the desired varieties of wheat were consequently in demand and these substitutes also brought a considerable premium in price, ranging from 8 to 16 cents per bushel.

You will note, therefore, that any grain company, which by the service of its chemist may be able to pick up any quantity of these wheats so much desired by the millers will thus make a handsome profit above the expense connected with the operation of a laboratory.

The extension of the wheat and flour testing will undoubtedly be determined by: (1) The ability of the chemists to agree upon a uniform method for conducting the testing and in expressing their results; (2) the ability of the chemists to convince the grain dealer and the miller of the profit which may be derived from a satisfactory knowledge of the wheat being purchased.

HOW TO IDENTIFY ROSIN AND GLUE SIZINGS.*

In a contribution from the Royal Testing Laboratories of Germany, which is abstracted briefly in the *Papierfabrikant*, Prof. W. Herzberg draws attention to the work of Kollmann on the testing of papers for the detection of rosin and animal sizes. Kollmann has determined the behavior of papers in the presence of various reagents, including iodine solution, concentrated nitric acid, nitrate of mercury, potash lye and sulphate of copper. (Biuret reaction), glacial acetic and concentrated sulphuric acid (Adamkiewicz), tannin solution, concentrated sulphuric acid and sugar (Raspail's reaction). Only Raspail's reaction and the tannin reaction were found useful, and these only in the absence of fat and casein.

The Raspail Test.—The Raspail test depends on the fact that proteids, rosins, fats, etc., turn rose colored or violet under the action of concentrated sulphuric acid, and a little strong cane sugar syrup. Animal size shows the reaction much weaker than rosin size, so that the reaction only comes into question for the recognition of the latter. The test can only be carried out satisfactorily under the microscope.

The procedure is to dampen a little scrap of paper with the sugar solution, put it on the slide, free it from excess of sugar by lightly pressing blotting paper on it, and then to add the strong sulphuric acid when the paper is already under observation with a low power. In this case nothing much will be seen if the sizing is animal, but with rosin sizing a deep red color will appear at the parts of the paper attacked by the acid.

The Tannin Test.—Tannin precipitates animal size. If a piece of paper is wetted and stuck on the slide, and warmed, the paper being then removed, and tannin solution added to the aqueous extract left on the slide, no precipitate appears if the size was rosin, but a voluminous brown deposit, readily observed as it appears through the microscope, is formed in the case of animal size.

Extraction Tests.—Some of the other tests commonly employed in the determination of rosin and glue in papers are as follows: The United States Bureau of Standards determines the rosin quantitatively. A 5 gm. sample of paper is cut into strips and the paper folded back and forth upon itself, and then placed in a 300 cc. Erlenmeyer flask. The paper is extracted with alcohol made acid with acetic acid.

The extract is next transferred to a casserole and after evaporating off the alcohol, the acid residue is taken up in water and extracted with ether in a separatory funnel. Three extractions are sufficient and the combined ether extracts are washed twice with water and transferred to a weighed dish. After evaporation to dryness the residue is evaporated with absolute alcohol to remove water and heated in an air bath at 90° C. for one hour.

*From Paper.

The dish is then allowed to cool in a desiccator and weighed. The resultant weight in grammes divided by 5 and multiplied by 100 gives the percent total rosins.

One of the simplest tests for the presence of rosin sizing is to place a drop of ether on the paper. The presence of rosin sizing will be indicated by the formation of a ring around the edge of the spot after the ether has evaporated.

A quantitative determination for glue may be made by extracting a sample of the paper with warm water and precipitating the glue with tannin or phosphomolybdic acid. The precipitate that forms is an indication of glue in the paper.

Of the foregoing test, described as used by the Bureau of Standards, Kollmann says that a test of this kind which depends on extracting rosin from paper with solvents that will not dissolve animal sizes, has, like the Kiliani test, failed so completely as to be negligible.

The Iodine Test.—The iodine test is approved by Kollmann. Albuminous bodies, which include animal glues, give with iodine solution either direct or, on acidifying with acetic acid, yellow or brown colorations or precipitates. The iodine solution is made by dissolving as much iodine in a 1 per cent solution of potassium iodide as possible. The reaction must be observed not only with the sized fiber, but with an aqueous extract of the paper. If some of the paper, teased out with a needle on the slide, is dabbed with the solution, a brown color is produced, whether the sizing is rosin or animal. If, however, the paper is heated on the slide with a little water, and then removed, the dried residue on the slide shows characteristic appearances under the microscope and even under a good hand lense.

Animal-sized paper leaves behind a considerable structureless residue extending over the whole surface formerly occupied by the water. The iodine solution gradually dissolves it with a rusty red color. On the other hand, rosin-sized paper leaves but little residue, and that shows a grainy structure with an irregularly dented edge round the space formerly taken up on the slide by the aqueous solution. This residue also gives a brown color with the iodine solution. It consists of free abietic acid, melted out by the hot water, and forming an irregular deposit against the dry part of the glass.

The Xanthoprotein Reaction.—The nitric acid test affords the so-called xanthoprotein reaction, albuminous bodies giving a more or less pronounced yellow color after heating with nitric acid and subsequent exposure to ammonia. Many rosins and alkaloids react similarly. The test is applied as follows:

A small piece of the paper is treated on the microscope slide with strong nitric acid, carefully dried, and then treated with ammonia. If the paper was sized with animal size, the yellow will be deeper. The dif-

ference is small, but with practice it can be safely used to distinguish between animal and vegetable size.

The Millon Test.—When warmed with this reagent (a solution of mercuric nitrate containing nitrous acid) all albuminous bodies, and, therefore, animal size, are colored red, from a light pink to a deep brick red. The reagent is best prepared shortly before use by dissolving one cubic centimeter of mercury in 9 cc. of nitric acid of 1.52 sp. gr., and diluting the solution with 10 cc. of distilled water. The test is applied as follows:

To a few drops of the solution in a watch glass add just the smallest possible fragment of sodium nitrate, to insure the presence of enough nitrous acid. A drop is then transferred by means of a glass rod from the watch glass on to a scrap of the paper to be tested on the slide, which is then carefully heated. In the presence of albuminous bodies, the paper turns red, the shade being pale or dark according to the amount of size present. The red soon changes, however, to a dirty brown, and if the Millon reagent is not fresh, the characteristic pinks and reds may be lost altogether. This yellowish brown is the only color produced by the reagent in the case of rosin size. This test, too, is only reliable in experienced hands.

The Adamkiewicz Test.—If albuminous bodies are warmed with a mixture of two parts of glacial acetic acid and one of concentrated sulphuric acid, many of them give a strong red or violet coloration. Casein shows this reaction, animal size does not. This test can only be applied to an extract made from the paper with dilute potash. The paper is wetted with the lye on the slide, and then removed with a needle. The remaining liquid is made acid with acetic acid, and warmed to coagulate the casein. This is then washed by alternate moistening with water, and pressing with filter paper. It then gives the color with the mixed acids.

The Biuret Test.—Albuminous bodies treated first with caustic potash lye, and then with solution of sulphate of potash, give colorations of red and violet. The value of this test consists in the fact that it gives a fully negative result with rosin size. This test is also best tried under the microscope. A little bit of the paper is wetted on the slide with caustic potash lye of about 10 to 15 degrees B., and after a minute or two has been given to enable the caustic alkali to dissolve the size, one drop of a 2 per cent solution of copper sulphate is added from the end of a glass rod. The violet shows best in the fiber after the slide has been drained by setting it on edge.

Kollmann advises that the tests should be carried out on the stage of the microscope whenever possible, so that the colors and precipitates can be observed as they form. The colors are very fugitive, especially under the strong light from the mirror below the stage. If the presence of both sorts of size is suspected, care must be taken to test for them on different portions of the paper.

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NOTES AND COMMENTS.

Dr. Ira Remsen Receives the Williard Gibb's Medal.

The members of the Chicago Section of the American Chemical Society, together with invited guests, met at the Hotel Sherman on the evening of May 15 to present the Williard Gibbs Medal to Dr. Ira Remsen of Johns Hopkins University. This was the fourth presentation of the medal, which was founded by William A. Converse in January, 1910.

Dr. Remsen selected as the subject of his address "The Development of Chemical Research in America." Perhaps no person in the country is better qualified to speak upon this subject, his remarks, therefore, were intensely interesting. Dr. Remsen mentioned the fact that chemical research in this country, until about 1876, was sporadic, but shortly after this, owing primarily to the foundation of Johns Hopkins University, and the formation of their graduate department for chemical research, chemical research in America commenced to be epidemic. Personal mention was made of many of the earlier workers in chemistry in the country and some attention was paid to their work, particularly as to its effects on succeeding research.

The presentation of the medal was made by Dr. W. A. Noyes, Professor of Chemistry at the University of Illinois, and a former student of Dr. Remsen. Following the address of Dr. Remsen, there were short addresses given by President Harris of Northwestern University and President Vincent of the University of Minnesota.

The occasion was a very pleasant and memorable one and we expect to publish in our next issue an abstract from Dr. Remsen's remarks on this occasion.

Alcohol as a Motor Fuel.

As a result of the Imperial Motor Conference held in London in July, 1913, an organization known as the Imperial Motor Transport Council has been formed and the council in turn is forming an alcohol motor fuel committee, which will conduct investigations and experiments relating to the use of alcohol as a motor fuel.

In a paper read recently before the Institution of Automobile Engineers it was stated that the principal objection to the use of alcohol is its low heating value. It is claimed, however, that this can be overcome by mixing a certain amount of benzol with the alcohol. One of the chief deterrents to the use of alcohol as a motor fuel in the United Kingdom is the excise restrictions imposed upon its manufacture; another is the lack of a suitable engine. It is believed that as soon as the use of alcohol is proved to be commercially practicable by automobile manufacturers, the restrictions may be either considerably modified or so far removed as no longer to form a hindrance to its adoption for commercial use.

It is reported that a plant for the manufacture of 600 gals. of alcohol per week is being sent out to a British colony; the spirit will be made from corn costing \$3.88 to \$4.63 a ton, and it is believed that the cost of raw material will not exceed 6 cents a gallon and that the total inclusive cost will be less than 18 cents a gallon. In the meantime it is claimed that a fund should be raised to demonstrate how cheaply alcohol can be manufactured on a large scale, and that designers should turn their efforts to the construction of efficient engines for use with alcohol.

The author of the paper read before the Institution of Automobile Engineers claims that the modern high-speed gasoline engine would run on a half-and-half mixture of benzol and alcohol with as much power, flexibility, ease of starting, silence, and economy as with its ordinary gasoline fuel, and with merely slight modifications to existing types of carburetors.

Manchurian Soya Bean Production.

Investigations made by the South Manchuria Railway show, states Consul Albert W. Pontius, Dalny, Japanese Leased Territory, the 1913 season crop of soya beans about Changchun, Kungchuling, Kaiyuan, Taolu, and Shanchengtzu to be of fine quality, this zone having experienced favorable weather. On the other hand, the belt lying between Liaoyang and Tashilchiao and along the Mukden-Antung Railway suffered to a considerable extent from drought, and the yield in that district is reported generally as of poor quality and likely to be less than 50 per cent of a normal harvest. In October new beans of good quality were quoted on the Dairen (Dalny) market at \$2.02 per 100 kin of 132.3 pounds.

OUTPUT OF BEAN CAKE.

The daily combined output of bean cake at the Dairen mills has heretofore been estimated at 70,000 pieces. The establishment of four new mills and the reconstruction of the Santai bean mill will increase the daily output to 100,000 pieces. During 1912 a total of 10,503,595 pieces of bean cake was produced at the local mills, and as each piece weighs approximately 62 pounds, the output was in excess of 325,000 short tons. About 300,000 tons were shipped to Japan, the remainder finding its way to South China ports. Of the 51 bean mills now in operation, 6, owned and operated by Japanese, produce two-thirds of the total output.

MOTIVE POWER FOR MILLS.

Two Japanese and seven Chinese bean-oil mills at Dairen have recently altered their motive power from petroleum to steam. Hitherto electricity, gas, and petroleum were in more popular use than steam, but a comparative study of the cost of machinery operation by the different kinds of motive power, instituted within the past year, showed that for each 62-pound piece of bean cake manufactured the net cost of electricity and gas was 7 mills United States currency, petroleum 5 mills, suction gas 4 mills, and steam $2\frac{1}{2}$ mills. As the use of power other than steam necessitates the installation of special equipment for steaming beans, this feature gives steam a decided advantage over other kinds of motive power.

Bulletin on Linen, Jute and Hemp Industries.

An illustrated bulletin on the linen, jute, and hemp industries of the United Kingdom, with notes on the growing and manufacture of jute in India, will soon be available for distribution. The bulletin was prepared by Commercial Agent W. A. Graham Clark and is issued by the Bureau of Foreign and Domestic Commerce as Special Agents' Series No. 74. As linen manufacturing centers largely in Ireland and jute manufacturing in Scotland, special attention is given to these industries in their respective fields. Detailed information is presented as to processes of manufacture, cost of production, wages and condition of employment, cost of constructing and operating factories, commercial usages, and foreign trade.

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THE DEVELOPMENT OF CHEMICAL RESEARCH IN AMERICA.*

By DR. IRA REMSEN.

The subject which I have chosen is stated upon the menu "The Development of Chemical Research in America." That is a subject upon which I might talk for a week. I have recently, since I selected this subject and sent this title to your chairman, read a book which appeared within a few weeks called "Chemistry in America." I had seen notice of its publication, but did not read the book until after I chose this title. The book is prepared by Provost Smith—or Professor Smith, as we prefer to call him—of the University of Pennsylvania. I have read that book from one end to the other and it gives in detail the course of chemical research in this country. There it dwells at great length upon a few researches which, except from an historical point of view, are of no special value. Now it is not in that way that I want to treat this subject. I want if possible to point out the conditions under which research developed and became what it is today—epidemic. It was sporadic for many years, but it later became epidemic and is now, in fact, in the most acute stage.

Of course there was not much research in the 18th century in this country; there was not much in Germany. In fact Liebig tells the story of the condition of affairs in Germany at the beginning of the 19th century and he uses the expression, "It was a poor time for chemists in Germany." That was as late as the 20's in the 19th century. He had to leave Germany to study his chemistry in Paris and from Paris he went to Sweden to continue his work. It is very interesting to note that the leaders of that time had to leave Germany, which we now look upon as the leading country for this knowledge, in order to get any satisfactory training. I say it is not surprising that there was not much chemical research in this country at that time. There were many other things to do.

We were very busily engaged in trying to form a nation and develop material resources. Nevertheless, during the last part of the 18th century there were a few men who tried their hand, and at the commencement of the 17th century there was a fair start made.

The latter part of the 18th century there came to this country one of the great chemists of the time, Priestley. He arrived in Philadelphia in 1794. I suppose you all know that he came because he was very badly treated at home on account of his religious views. He settled in North Cumberland on the Susquehanna River in Pennsylvania. He was in correspondence at that time with those who were in control of the University of Pennsylvania, and he was also in correspondence with Jefferson. They tried to persuade him to come to the University of Pennsylvania, but he finally decided not to accept active work, but to retire after his troublous times in England and live a quiet life somewhere in the country. I mention Priestley because he was the first distinguished chemist of this country, but it is evident that Priestley's work did not have much effect on chemical research in this country. He devoted his entire attention to theological questions.

The influence which was strongest in this country at that time was that of Franklin. Franklin had produced a profound impression upon a certain group of people in Philadelphia and the greatest amount of scientific activity shown in this direction at that time was in Philadelphia. We find from that time on that the leading chemists were those who actually came from that city. I will not go into details in the matter, but I cannot help but mention the name of one who has been prominent in that group, Robert Hare. Robert Hare, I should judge from all that I can gather from his writings, was really a very remarkable man. When he was but 20 he invented a compound blow-pipe in which we utilize the affinity between hydrogen and oxygen and get that intense heat which is the result of their combustion. That was a remarkable achievement for a young man of twenty. It required a great deal of courage, ingenuity and perseverance to devise such an apparatus. This apparatus has been of very great importance to mankind ever since. I came upon an article by Robert Hare in the course of some work I was doing some few years ago; I wrote an article which dealt with the so-called double halides. After that article was published I received a letter from another chemist, one of the older set, telling me that Dr. Hare had expressed some similar views in 1821. Now Dr. Hare's name was not known to me at that time. I did not know he was the in-

*Abstracted from an address delivered May 15 before the Chicago Section of the American Chemical Society.

ventor of the oxy-hydrogen blow-pipe. I asked my correspondent where I could find the articles of Hare and he sent them on to me. I was astonished to read the article that he had written 50 or 60 years before mine, in which the line of thought was practically identical with that which I had expressed in different terms, but it was expressed beautifully and I should have been glad to treat the subject as well as he did. I have felt a very strong sympathy with Hare since that time. Now that man was active in Philadelphia in 1810 and later than that also. He was a professor, if I remember correctly, in the University of Pennsylvania; nearly all the chemists in those days were. Robert Hare remained the leading chemist of this country for years. I do not find that he added very much to the material that I have already referred to, but he was evidently a broad, clear thinker and a man who helped the cause wherever he had to deal with it.

The names that come to my mind next are Booth, who was an analytical chemist, but a remarkably skillful one in connection with the chemical part of iron and steel—a very big man. I think he died a few years ago. Then there was Sterry Hunt. He was something of a philosopher, somewhat of an experimentalist also. His work covered a very wide range, organic chemistry, physical chemistry; anything that came along was grist for his mill. The trouble was we could not understand him, but he really advanced the cause. Then there was J. Lawrence Smith. The latter part of his life was spent in Louisville. He was an investigator and always stood for high ideals in that line. One thing that we retain from his labors is his method of determining alkalis, which I believe is still the best method used. Lawrence Smith left a considerable fortune and some of that was for the purpose of encouraging research on meteorites.

We come now to two men who stood out very prominently as investigators. I remember in my youth when I thought of studying chemistry those two names always loomed up as those of *investigators*, but what they investigated or why they investigated it I did not know. They were Wolcott Gibbs and Fred Genth. Those two men, and especially Wolcott Gibbs, were the strongest influences to keep chemical research alive in this country. Gibbs was one of the highest minded scientific men I have ever known. I remember studying at a school where he was then the teacher, and the first glimpse of chemistry I got I had from him. He was born in 1822 and died in 1908. I remember this: Some one of the boys at school had heard it said that Gibbs was a great man. I had a fondness for great men and was curious to know why he was considered great. I asked my friend, "Why is he a great man?" "Oh," he said, "he's just a great man, he can't help it." I attended one lecture a week for four years and the only thing I can clearly remember from those lectures is the word sesquioxide. This impressed me very strongly. Gibbs was a great man in a way. He was great in this respect, that he

never wavered in his loyalty to true science. He was true to his convictions to his last day. I visited him in Newport in the last days of his life and he took me out to his private laboratory. This was in 1905 or about that time—two years before his death. He told me then of ideas he had for new work. No one can overestimate the influence of Gibbs on the cause of true science in this country. Genth was a different mould of man, an able man. He was a good jolly German. He came to this country, I think, in '48, and established a commercial laboratory and his business through life was to do analyses for people, but during that time he also carried out an investigation with Gibbs which is known to all chemists and laboratory research workers, on the *cobalt ammonia bases*, in which they brought out a large number of compounds that proved to be of very great interest, and which set people to thinking. Now the chief advantage or merit of that investigation was the fact that it impressed upon the minds of young men the idea of the possibilities of creative work in chemistry. What it was all about we did not know, but it was placed before us, and although that investigation has never been regarded as a great investigation, it did have marked influence upon the lives of a good many young men. Genth afterwards became president of the University of Pennsylvania in 1872 after the university moved from its old site to its present location.

At that time, or just before, there was a Professor Cooke of Harvard who was a thorough scientific man, a thorough scientific worker, a man always true to the highest standards of science. There was Professor Johnson, who was one of the prime movers in agricultural chemistry in this country, one to whom we owe our experimental stations. There were other men working about the period of which I am speaking, but I have not the time to go into details.

Now I come to an extremely important time and I suppose it will be better for me to sit down and say nothing more. I probably should leave this room with a better reputation if I said nothing. The point is that I come to a time when I am obliged to refer to myself.

I came back from Germany in 1872, having spent five years of my life there. There I had an opportunity to become familiar with the German methods. I became enthusiastic and imbued with the notion that that sort of thing was something we needed in this country. I pointed out that we had investigators in this country, but the investigations up to the time of which I speak were sporadic. On arrival in this country I discovered that it was very thickly populated. I did not realize how thickly populated the U. S. A. was nor how thoroughly filled all the places for young men were and I passed a very dark summer wondering what was going to happen to me.

One of the first things that offered was a professorship of physics and chemistry in Williams College, Williams, Mass. That I accepted a professorship of

physics shows that I had a good deal of courage. It was not what I wanted but I accepted it and kept a bold front and passed through four years of professorship in that little country college. I am very glad I went, and had the four years' experience in a college of that kind. I made lifelong friends there and became familiar with an American college, and altogether the experience was one which I prize very highly, but looking at it from the point of view of my scientific ambitions it was the most deadening influence that can possibly be imagined. I succeeded in getting a room 10x8 ft. where I installed my laboratory.

Then came the founding of the Johns Hopkins University in Baltimore. Its great object was scientific research, and I was tendered the professorship of chemistry. There was opportunity. I was told by the president of the university, "Do your own work in any way you please. You will not be interfered with by anyone." We do not get orders like that every day. I bought all the apparatus I wanted and all the books I wanted. We had no students. I got two or three young men together and we began work. Now I am well aware of the fact that chemistry was not revolutionized nor was anything else, but we made the start. Then we came to publish our material, the articles which were the result of this investigation. I sent the resume of our first series of articles to the American Journal of Science at New Haven. I had been sending my sporadic articles to Professor Dana, but when I sent this large batch in a few days I got back word that it would be necessary for me to find some other place to publish my articles, as they seemed too highly specialized and too voluminous for a journal of general science. Professor Dana then suggested that I start a journal myself. In 1879 I started the American Chemical Journal and it lived until January, 1914, when I passed it over to Professor Noyes.

This experiment made in Baltimore in 1876 had an important effect upon the country, that is, upon the chemistry of the country, and chemical research became then epidemic. Today we have a number of centers of work in chemistry that are far superior to the center that caused the trouble—the one that began work in 1876. That was the turning point in the history of chemical research in this country. Mind you, I am not making any comparison as to the value of work done, but I am simply pointing out the beginnings that led to the movement that has reached on to the present stage.

The work was carried on by Professor Smith in the University of Pennsylvania. Mallet continued the work in the University of Virginia in a true scientific spirit. Then somewhat later we come to the great University of Chicago and the University of Illinois, almost side by side, the University of California, the University of Wisconsin and other institutions, in Chicago and elsewhere, are doing a great amount of chemical research work today. Progress I thought

almost impossible to make within any reasonable period has already been achieved.

I have simply tried in a sketchy way to indicate the general character of the advance. I fear I have over emphasized the part that was played by the Johns Hopkins University, but I do believe that that was the turning point. The opportunities given us young men there (I was 30 at the time) led to opportunities being given to young men and old men elsewhere. That was the thing that was of chief importance in that movement and rivalry has grown up among those engaged in chemical research, and we have all reason to be proud of the present condition of affairs in this country.

THE STORAGE OF COAL: ITS FEASIBILITY AND ADVANTAGES.*

By C. C. HALL†

This paper proposes to discuss only the storage of bituminous coal, and as each coal field of the world has internal and external conditions peculiar to itself, that part of my remarks relative to market conditions and sizes of coals will be directly applicable only to the coal districts adjacent to Chicago, Indiana and Illinois.

The "deplorable condition" of the bituminous coal industry has been emphasized by the coal operators in all conventions and meetings in which they have participated during the past 18 months. Remedies have been proposed, discussed and abandoned as impracticable or unlawful. It has even been proposed, in conventions of national scope, that Congress be petitioned for an appropriation to put the bituminous coal industry on its feet financially. However, it has been apparent that the majority of producers do not yet feel that they should be placed upon the Government's pension list.

The carriers have contributed somewhat to the overproduction by building lines into new fields and making lower rates on long hauls, moving coal beyond the economical zones and pouring it into already flooded markets.

The carriers have in the past come in for a great deal of criticism from the producer and the consumer for their inability to furnish cars for loading all the coal which the mines could produce during certain periods of abnormal demand. If they were to put themselves in position to furnish a full supply of cars at all times, and maintain prompt movement, it would sound the death knell of high mine prices and put a goodly portion of the coal companies out of business. It is hardly consistent, however, to ask the carriers to go to this enormous needless expense in order to close up the surplus mines and add to the delivered price

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of coal the fixed charges incident to such an investment.

The storage of coal in the summer months will enable the carriers to move a percentage of the tonnage during that season, which they are now called upon to move during 60 or 90 days of each fall and early winter, and during which period no railroad in this country now has nor ever can afford to have, sufficient power and cars to serve the mines and move the coal to accord with the demand. To do this, we will say, five of the large coal moving roads of Illinois and Indiana would each have to buy 50 new locomotives and 6,000 new coal cars:

A total of 250 locomotives at \$25,000.....	\$ 6,750,000
A total of 30,000 cars, at \$800.....	24,000,000

A total investment of.....	\$30,750,000
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The annual interest on which, at 5 per cent, would amount to \$1,537,500, and a great percentage of such cars and power would be idle eight months of the year.

This is only a small portion of the total investment that even this small group of railroads would have to make in order to handle the coal as the consumers now demand, as the expense of additional double and triple tracks and yard facilities would far exceed the cost of additional equipment and power. It is, therefore, very apparent that the carriers would have to spend so much money to provide 100 per cent car service during the short abnormal offerings of coal that a substantial increase in freight rates would be the inevitable result which, of course, would mean an increase in the ultimate delivered cost of the coal. Thus the consumers would not only be called upon to pay the interest on an excessive amount of capital invested in mines, but would also have to carry the burden of an excessive investment in equipment and facilities on the part of the carriers. Will the producers and coal-consuming public please bear this in mind, and not condemn the carriers too harshly the next time there is a coal-car shortage?

The only curb on the excessive production of coal has been the inability of carriers to provide and move sufficient equipment to give the mines full running time, and the further curtailment which has resulted from the miners demanding and securing a shorter working day. Right here it will not be out of place to say that the miner has demanded and secured a higher rate of pay, which gives him a higher daily wage than he received when working a greater number of hours, with the result to the operator of a reduced daily output and a material increase in the cost of labor per ton.

This is an unnatural condition, and there is no question but what some feasible arrangement will have to be made for storing bituminous coal, as an industry of the magnitude of the coal operations of Indiana and Illinois alone cannot hope to continue to exist and compete in this economical age on the basis on which it now exists. Some means will have to be provided to

enable the mines to operate 300 days per year instead of 175 to 225 days, as now obtains.

The storage of coal will not increase the consumption of coal, and may ultimately result in closing down unprofitable mines; but it will discourage the opening of new mines until such time as the demand—which, of course, is governed entirely by the consumption—will justify the opening of new mines on a profitable basis. In other words, instead of the coal business being a gamble, as it has been for the past 10 to 15 years, the storage of coal by the domestic users, the dealers, the industrial plants and the railroads, will give the mines fairly equal running time throughout the year, making coal one of the staple products of the country, as it should be.

It is needless to comment on the fact that more uniform running time is the one thing essential to the successful operation of the mines, but in addition to enabling the operator to produce coal at the minimum cost it will also give him better satisfied labor, and do more to eliminate the "walking delegate" than all the suspensions that have taken place or that may be brought about in the future. It will also have the effect of postponing, and possibly removing, the cause for the miners demanding a shorter working day than now exists, with a corresponding increase in the mining rate and day-wage scale, so that their daily compensation will be as great or greater than at present.

The individual domestic consumer has never been brought to realize that his present system of demanding his winter supply of coal in October or November has a very material influence on present conditions, so far as car shortages and the necessity of coal operators maintaining more mines than the actual yearly consumption will justify are concerned; and the desire of the individual consumer "to have what he wants when he wants it" is one of the greatest factors in creating and maintaining the unsatisfactory conditions which now exist in the bituminous coal industry.

The logical and most economical method of storing coal is at the ultimate destination and a strong effort should be made to bring the householder to realize that there is no other small item in his living expenses that will pay as big returns on the investment as to lay in a winter's supply of coal in May or June, when it can be procured at a price ranging from 50 cents to \$1.00 per ton cheaper than it can in October and November, when he ordinarily demands it. He will also quickly learn that it is not necessary to have all large lumps in order to secure satisfactory results in boiler or furnace.

However, we will always have with us the improvident class, and central storage yards are necessary to help protect their requirements. The higher cost incident to handling through storage plant, and the increased expense of transportation, should in all fairness be borne by the consumer who demands his coal as it is used.

It is only reasonable to suppose that if consumers are asked to co-operate with producers and carriers to the extent of storing some coal during the spring or summer they will expect to be shown wherein they will be benefited; this also holds true in the case of dealers or jobbers who may plan to go into the storage proposition on a large scale.

The producer has in the past, and will unquestionably in the future, make sufficient price concessions during the spring and summer months to make an attractive feature of storage.

The carriers should also offer inducements in the nature of freight rates, with "storage in transit" privileges, and should make lower rates during the months that it is to the advantage of all interests to store coal.

The total operating expenses of the railroads moving the Illinois and Indiana coal to Chicago and the adjacent territory north and west show an increase of 31 per cent in proportion to gross earnings in a severe winter month as compared with a spring or summer month. It is, therefore, entirely fair, in fact a sound business proposition, for these carriers to make a corresponding variation in freight rates. For example, the present rate to a given point is \$1.00 per ton; why should not a rate of 85 cents be made for the months of April, May and June; 95 cents for July, August and September, and \$1.10 for the remaining months of the year?

In event of coal being put into storage during the spring or summer months, at Chicago for instance, and then reloaded and forwarded to a final destination in the fall and winter, the freight tariffs could provide for a rate from mines to storage yards equal to the proportionate rate to Chicago at the time the coal moved. The lines handling the coal to destination could put in tariffs from Chicago storage piles to points beyond, based upon the proportionate rates beyond, so that the storage company would get the benefit of the reduced summer rates from mines to Chicago, and would pay the prevailing proportionate rate beyond at the time coal moved out of storage.

This differential in freight rates, together with the producer's price concessions, should certainly give the consumer a margin, as compared with boom prices of the fall and winter, that would make the storage of coal an attractive proposition.

As stated earlier in this paper, the operators of Indiana and Illinois have been very apathetic toward the matter of storing coal; however, there is no question but what the producers and carriers will have to work out plans and be able to show the consumer that it will be the means of saving him some money before he will take any action in that direction.

While unquestionably the best and most economical results can be obtained by moving the coal to final destination before storing, it may be desirable and necessary to establish storage yards at principal distributing centers, such as Chicago, Peoria, St. Paul and

Omaha, and, in doing this the co-operation of producers and carriers will be essential. In fact, it would probably be feasible and desirable for the producers to control the storage companies.

These central storage yards should have a capacity of 100,000 to 500,000 tons, a screening plant to be installed in conjunction with the yard. The screening plant could be patterned after those now in use by the dock companies, which screening plant is movable. This screening plant is fed by the grab-bucket from the stock-pile, and three sizes of coal can be screened. The different sizes can be fed directly into cars, and the screenings into gondola cars or to stock-pile. There is a box-car loader fixed on the pier of the rig under the screening plant. The coal that is carried out into the stock-pile after going through the screening plant has to be picked up again with the bucket.

If this style of plant is too elaborate and expensive a simpler and cheaper arrangement can be made whereby the coal is unloaded from cars by means of a bridge and traveling clam-shell bucket, and reloaded by the same machine. A stationary screening plant could then be installed, the coal to be dumped into a hopper and hoisted to the screens by means of a bucket conveyor-chain, balanced buckets or conveyor-belt.

Electrical power would be desirable, in fact almost essential; however, this is an advantage rather than a drawback, as such power would be available at all points where it would be desirable to install a general storage yard, and it would be cheaper than any other power.

By means of car-pullers it can be arranged for the cars unloaded over the receiving hopper to move in the opposite direction from those under the screens, so that the empties from the hopper track can be returned immediately under the tipples, thereby curtailing the switching and minimizing the number of railroad cars required to operate the plant.

A similar screening plant may be used in connection with a storage yard where the coal is unloaded and reloaded by the use of locomotive cranes. A plant of this type does not provide the storage capacity of those previously mentioned; however, it has advantages in the fact that coal can be more readily graded when storing and, in event of the fire the trouble would be restricted to a limited area and the coal moved quickly.

There are numerous devices for storing and recovering coal from storage that are very efficient and entirely practicable. Furthermore, any one desiring to store coal will find the manufacturers and contracting engineers ready to co-operate to develop and perfect devices and machinery to meet any conceivable condition.

The railroads of this country, as consumers of approximately 25 per cent of all the coal produced, are vitally interested in perfecting arrangements for the systematic storage of coal each year.

Beyond their interest as consumers they are also deeply involved in the coal industries as carriers, and,

as outlined in some of my previous remarks, the storage of coal at the proper seasons will fit into the operations of the carriers so that not only will they be able to amply protect the movement of coal with the equipment now in service, but they will be in position to deliver it at a lower cost than if they are compelled to provide equipment and facilities to meet the fitful movement that has prevailed in the past.

In storing coal the railroads should plan, as far as practicable, to move it to final destination before unloading, in order to save the use of cars at the time when the coal is to be used. To do this most effectively the coal should be stored at the coaling stations and arrangements made to recover it without involving the use of cars. This can be done by planning storage space and devices for handling the storage coal at the time the coaling station is installed.

A coaling station, handling 300 tons daily, located 150 miles from the mines or the delivery point of connecting line will require as a minimum 45 coal cars to provide a safe working supply of coal.

At a time when the demand for coal is great each car is worth more than \$2.00 per day; but in this instance we will say \$2.00 per day. Forty-five cars at \$2.00 equals \$90.00 per day, and for 60 days—which is about the average period of the fall rush for coal—it would amount to \$5,400, repaying the company for the storage layout in two seasons. The 45 coal cars would represent an investment of approximately \$35,000, so the question of interest on the investment is all in favor of the storage facilities. In addition the railroad company would secure the benefit if the reduced expense of moving the coal during the dull period of the summer and avoid, to some extent, the congestion which prevails in the fall, due to the heavy movement of grain and the abnormal movement of coal.

There is still another factor, i. e., at the time the railroads are storing the coal, which should be either egg or lump, the mines are producing nut and slack—representing from 38 per cent to 60 per cent of the volume of coal stored—for the commercial market, giving the railroads this additional tonnage at a time when they need the traffic and can move it at the lowest cost.

As the distance from the coaling stations to the source of supply increases so also does the amount of the saving resulting from the storage of coal increase, and I am satisfied that if the managements of our railroads will give this subject careful study they will realize that a car is the most expensive receptacle for company coal during a car shortage period, whether it be held at the coaling station, in transit or at the mine, and that a little money judiciously spent for storage facilities will answer the same purpose as a large expenditure for cars and locomotives.

In the absence of sufficient space adjoining coaling docks already installed or to be constructed to permit of such a storage arrangement as has just been described I would recommend the use of locomotive

cranes, the storage ground to be located as near the coaling station as practicable, taking all conditions into consideration, such as accessibility for switching, protection from theft, etc.

An arrangement of this kind necessitates the use of some cars when recovering the coal from storage, but it will only require about one-third the number required to serve the dock from the mines. The expense of unloading and reloading is very reasonable, as the experience of railroads that have at different times stored coal as a protection during strikes or suspension of work at mines develops that the work can be done at a cost of 10 cents per ton, including cost of tracks, interest on investment for cranes and all other items entering into the expense.

Contrary to the common belief, coal does not suffer serious losses when exposed to the elements. Exhaustive tests and researches have been made by the University of Illinois and the Bureau of Mines, and the bulletins issued indicate that the calorific loss on coal exposed to open air for one year or more is not sufficiently great to make the storage of coal prohibitive. I refer* particularly to a series of tests conducted by Prof. S. W. Parr and W. F. Wheeler, of the University of Illinois, and I am taking the liberty of quoting the following from their conclusions:

TABLE I.—ACTUAL EXPENSE, ONE RAILROAD, UNLOADING AND RELOADING, THREE STATIONS, 1913.

Station.	Tons.	Unloading.				Total	
		Avg. Cost		Supplies.	Track.	Cost.	Avg.
		Labor.	Labor.				
"G"	9870	\$293.23	.0297	\$27.10	\$179.27	\$499.60	.0506
"H"	9396	285.31	.0304			285.31	.0304
"T"	7373	175.76	.0238		198.77	374.53	.0508
	26639	\$754.30	.0283	\$27.10	\$378.04	\$1,159.44	.0435
		Reloading.				Total Cost of	
		Avg.		Supplies.	Total	Cost.	Avg.
		Labor.	Labor.				
		\$219.87	.0223		\$219.87	\$719.47	.0729
		203.41	.0216		219.41	488.72	.0520
		30.00	.0040		30.00	404.53	.0549
	\$453.28	.0159		\$453.28	.0159	\$1,612.72	.0604

Coal of the type found in Illinois and neighboring States is not affected seriously during storage when only the change in weight and losses in heating power are considered. The changes in weight may be either gains or losses of probably never two per cent in a period of one year. The heating value decreases more rapidly during the first week after mining, and continues to decrease more and more slowly for an indefinite time. In the coals that have been tested one per cent is about the average loss for the first week, and three to three and one-half per cent would cover the losses for a year.

A preliminary report† by Messrs. Horace C. Porter and F. K. Ovitz, covering their investigations conducted for the Bureau of Mines on the "Deterioration and Spontaneous Heating of Coal in Storage," contains some interesting and instructive information on the subject.

The disintegration of coal is a greater obstacle to storage than the losses in heat value, as there is no question but what the bituminous coals of this country will slack badly when exposed to the elements six

*Bulletin 38, University of Illinois, Engineering Experiment Station, 1909.

†Technical paper 16, Bureau of Mines.

weeks or more. This makes the re-screening plant a necessity where coal is stored in large units and subsequently recovered for the market. The re-screening plant described earlier in this paper provides for making four sizes; however, it may be found desirable to make only two sizes, i. e., 6-in. lump and egg; that is, all coal passing through the 6-in. openings to be used by the railroads on locomotives or in steam plants of industrial concerns, and the 6-in. lump to be utilized for the domestic trade.

Spontaneous combustion is the bugbear that has frightened and discouraged the storage-coal enthusiast more than any other one thing. Where coal is stored in small quantities there is very little danger, but when stored in large units great care is required to avoid spontaneous heating.

A recent Bulletin* of the University of Illinois contains an extensive and complete report, prepared by Prof. S. W. Parr and F. W. Kressman, of the results of their experiments and investigation of the question of spontaneous combustion of coal and all who are

*Bulletin No. 46, University of Illinois, Engineering Experiment Station, 1910.

Stored in Exposed Bins.	Dry		Coal to Actual Referred		Dec.	
	Ash	Sulphur	B.T.U.	Coal	B.T.U.	%
Same day as mined	15.26	4.03	12221	14787	...	...
7 days after mining	15.13	3.53	12164	14666	121	.82
2 months after mining	15.68	3.61	12024	14606	181	1.22
6 months after mining	14.96	3.36	12081	14525	262	1.77
1 year after mining	14.33	3.29	12065	14379	408	2.76
Stored in Covered Bins—						
Same day as mined	15.26	4.03	12224	14787	...	...
7 days after mining	15.13	3.53	12164	14666	121	.82
2 months after mining	15.07	3.53	12128	14605	182	1.22
6 months after mining	14.42	3.37	12105	14453	334	2.26
1 year after mining	14.77	3.57	11945	14323	464	3.14
Stored Under Water—						
Same day as mined	15.26	4.03	12224	14787	...	...
Same day as submerged	15.13	3.53	12164	14666	121	.82
6 months after mining	15.84	3.69	11937	14522	225	1.75
1 year after mining	15.02	3.81	12090	14567	220	1.40

a—The avoidance of an external source of heat which may in any way contribute toward increasing the temperature of the mass is a first and prime essential.

b—There must be an elimination of coal-dust or finely-divided material. This will reduce to a minimum the initial oxidation processes of both the carbonaceous matter and the iron pyrites. These lower forms of oxidation are to be looked upon as forces without which it would be impossible for the more active and destructive activities to become operative.

c—Dryness in storage and a continuation of the dry state, together with an absence of finely-divided material, would practically eliminate the oxidation of the iron pyrites.

d—Artificial treatment with specific chemicals or solutions intended to act as deterrents does not offer great encouragement, though some results seem to warrant further trial in this direction.

e—By means of a preliminary heating the low or initial stages of oxidation are effected. These sources of contributory heat being removed, the forms of destructive oxidation are without the essential of a high starting temperature, and are, therefore, inoperative. Whether such preliminary treatment is within the realm of practical or industrial possibility could not, of course, be determined within the scope of these experiments.

interested in this subject should secure a copy of this Bulletin. Their enumeration of preventive or precautionary measures to be considered when storing coal covers the situation so fully that to refrain from quoting from the same here would be passing this phase of the subject hastily:

Atmospheric temperature at the time of stocking is also a factor which should not be overlooked. With summer heat of 100° F., or greater, prevailing for six weeks or more during the time coal is being stored, and especially if the weather is dry during this period followed by a shower, and then further dry, hot weather, it has been the experience of one railroad that coal will fire spontaneously within a period of six weeks, even though it be large 6-in. lump and piled only four and five feet high.

It follows, therefore, that it is preferable to store coal in April and May, even though it is to be carried in stock until the fall and winter.

One million dollars spent by producers for storage facilities will afford more relief to the coal industry than five millions spent in the development of new mines.

The purchase of coal by the industrial and domestic consumers during the dull periods will result in a saving of a very high per cent on the investment.

NOTES ON NATURAL GAS PROBLEMS.*

By GEORGE A. BURRELL and FRANK M. SEIBERT.

In this paper are presented some results of the investigations of natural gases by the Bureau of Mines. Details of the experiments will be given later in publications of the bureau.

Experiments were made that resulted in the separation of natural gas mixtures into the individual hydrocarbons present. This had never been accomplished heretofore. Natural gases may contain methane as the combustible constituent or may be mixtures that contain large quantities of the higher gaseous paraffins. In addition there may be vapors of the liquid hydrocarbons present, sometimes enough to warrant the installation of a plant for the extraction of gasoline. The natural gas used in Pittsburgh is a complex mixture and is typical of gas that is supplied to many cities to the extent of billions of cubic feet per year.

It is generally known that ordinary combustion gas analyses give but little indication regarding the individual hydrocarbons present in a natural gas mixture. Only the two predominating paraffins are shown. The authors first liquefied natural gas by means of liquid air and then separated the different hydrocarbons by properly adjusting temperatures and removing the various fractions with a mercury pump. The fractions were then analyzed. Such a separation is possible

*Presented at the 9th annual meeting of the Natural Gas Association of America, St. Louis, Mo., May 19, 20 and 21, with the permission of the Director of the Bureau of Mines.

because in the liquid condition the boiling points of the gaseous paraffins are rather widely separated. These boiling points follow: Methane, -160° C.; ethane, -93° C.; propane, -45° C.; N butane, 1° C.; iso-butane, -10° C. The two butanes were not separated. It was found that at a temperature of -185° C. to -190° C. (the temperature of liquid air) the methane could almost entirely be removed, only a negligible quantity remained behind. It was found that the vapor pressure of ethane (boiling point -93° C.) is so small at the temperature of liquid air that only an unappreciable proportion was obtained with the methane. The separation of the ethane was conducted at temperatures ranging from -150° C. to -140° C. At temperatures slightly above -135° C. propane has an appreciable vapor pressure, hence in carrying out the experiment it was found best to collect the distillate up to -125° C., thereby removing all the ethane and part of the propane. The propane was then held as a residue at a temperature of -140° C. In like manner it was found advantageous to treat the residue after the ethane separation at a temperature of -110° C., thereby removing all the propane and part of the butane, etc., and subsequently hold the butanes, etc., as a residue from two or more liquefactions at -120° C. All through the experiments distillates and residues were re-liquefied and fractionated in order to obtain the last portions of the particular hydrocarbon that was being sought. In no case could the last minute portions be obtained so the attempts at complete recovery were stopped when it was found that only such a small portion was being left behind as did not sensibly affect the percentage results. Details of this work will be given in full in a subsequent publication of the bureau. The complete analysis of the natural gas used at Pittsburgh by this method follows. There is also given an analysis of the same gas by the ordinary combustion method.

ANALYSIS OF PITTSBURGH NATURAL GAS.

Constituent.	Analysis by Liquefaction and Fractionation.	Analysis by Combustion.
	Per cent.	Per cent.
Methane	84.7	79.2
Ethane	9.4	19.6
Propane	3.0	
(a) Butane	1.3	
Nitrogen	1.6	1.2
Carbon dioxide	Trace	Trace
Total	100	100

Only traces of the paraffin higher than the butanes were contained in the butane residue.

From the foregoing fractionation analyses, and from earth pressures that exist in natural gas strata, from temperatures therein and from the critical constants of the paraffin hydrocarbons, it can be calculated that none of the essential constituents of the gas occur in the earth in the liquid condition. This is important because if present therein as a liquid it would be possible for a single subterranean reservoir to hold much larger quantities of gas than is possible if the gas is in the gaseous condition in the strata.

ALTERATION OF THE COMPOSITION OF NATURAL GASES IN MOVING THROUGH THE EARTH'S STRATA.

The following two combination analyses were made of natural gas obtained in the same oil and gas field in Oklahoma:

LAB. NO. 3835. GAS FROM THE GLENN SAND.

Depth of Sand, 2,000 feet.		Analysis, per cent.			
		CO ₂	CH ₄	C ₂ H ₆	N ₂
(1)		.3	57.0	44.3	..
(2)		.5	56.8	44.7	..

Numbers 1 and 2 are duplicate analyses and are given to show how the results could be reproduced.

LAB. NO. 3837. GAS FROM MORRIS SAND.

Depth of Sand, 800 feet.		Analyses, per cent.			
		CO ₂	CH ₄	C ₂ H ₆	N ₂
(1)		.4	84.2	14.0	.4
(2)		.4	84.7	14.2	.7

Sample No. 3835 was obtained from a deeper sand, the Glenn sand, than laboratory No. 3837. The latter was obtained from the Morris sand. In the Glenn sand, gas and oil occur together. In the Morris sand only gas is found at this place. This sand is 800 ft. deep. The Glenn sand at this place is about 2000 ft. deep. The analyses are interesting as showing the difference in composition between the two gases. That from the shallow sand contains less of the heavy hydrocarbons than does the gas from the deeper sand. In some gas fields oil is pushed as far upward as incoming water will force it. Gas, however, may rise of its own accord until it is stopped by an impervious strata or until it escapes into the atmosphere. The authors do not know whether water occurs in or below the oil strata that holds the Glenn sand oil. It is possible that the gas in the Morris sand coming primarily from the same origin as the oil and gas in the Glenn sand changed in character in ascending, causing a separation of some of the heavy hydrocarbons.

It will be noticed that the analyses of the Glenn sand gas, laboratory No. 3835, totals over 100 per cent. This is believed to be due to the fact that errors are introduced in some gas analyses because of the assumption that the molecular volumes of all gases are alike. There is no way of correcting these errors in the case of the analysis of the gas mixture just mentioned because the partial pressures or the exact quantity of each of the gases that comprise the mixture are not known, and because the densities of propane and butane have not been experimentally determined. The analyses show no nitrogen, but some is undoubtedly present.

RELATIONS BETWEEN THE COMPOSITION OF NATURAL GAS AND THE OCCURRENCE OF OIL IN THE SAME STRATA OR NEARBY STRATA.

Most of the natural gas samples analyzed by the authors that contain only methane as the combustible constituent have been obtained in regions where no oil is found. These are the so-called marsh gases, large quantities of which escape into the atmosphere from marshy beds, springs, bogs, morasses, etc. Marsh gases also escape from driven wells in certain districts in very large amounts. These gases are apparently

unassociated with oil in the earth and apparently never originated in a strata that contained oil. On the other hand, the authors believe that a natural gas containing other hydrocarbons than methane shows the presence of oil either in the same sand as that from which the gas escaped or in other sands in the same locality. However, the presence of natural gases that contain methane only as the combustible constituents are not an absolutely reliable indication of the absence of oil in the district. This is proven by the presence of a large body of methane gas in the Hogshooter field close to an oil pool.

It is certainly not an unwarranted stretch of one's imagination to state that separations of the natural hydrocarbons have occurred in the earth. Starting from a place of origin common to both oil and gas, there could have occurred during the ages that have elapsed since the deposition of the materials from which these hydrocarbons were produced repeated separations until there could finally result (in rare cases) a deposit consisting of methane only as the paraffin hydrocarbon.

EXTRACTION OF GASOLINE FROM NATURAL GAS.

There follows some results of observations and experiments made by the Bureau of Mines having to do with the extraction of gasoline from natural gas.

The production of gasoline from natural gas increased from a few thousand gallons in 1904 to almost 30 million gallons in 1913. The industry had its commercial inception in Pennsylvania around Tideoute, Titusville and Warren. It wasn't until the year 1909 that the industry assumed commercial importance. According to the U. S. Geological Survey, the increase in production of gasoline for the year 1912 over 1911 was 63 per cent. The authors estimate that the rate of increase for the year 1913 over 1912 was probably 143 per cent. At the present time there is a lull in the production. The gas used represents that which previous to the installation of plants for the production of gasoline was largely wasted.

The paraffin hydrocarbons that principally concern the natural gas gasoline operator are methane, ethane, propane, and the butanes, pentanes, hexanes and heptanes. The first four are gases at ordinary temperatures. The last three are liquids. The gases after contact with the oil in the earth bring with them from the latter the vapors of the liquid hydrocarbons. These vapors are carried along with the permanent gases in the same manner that water exists with air. After treatment in the natural gas gasoline plant where the capacity of the gases to carry the vapors is much lessened, these vapors are deposited. The quantity of gasoline vapors in any particular gas mixture is dependent upon the character of the oil in the sand, temperature and pressure conditions in the sand, porosity or closeness of the strata, intimateness of contact between gas and oil and other less important factors.

The pentanes, heptanes and hexanes are the only constituents of crude oil that at earth temperatures

have vapor pressures of such magnitude that they are distilled in quantity from the crude oil, hence they are the chief liquid constituents of natural gas gasoline.

In the case of those wells from which gas is drawn under reduced pressure for gasoline condensation, the three gases, methane, ethane and propane, invariably occur in the earth in the gaseous condition, and butane usually.

By itself the ordinary combustion analysis is of little use for testing natural gases in order to determine the suitability of the gas for gasoline condensation. Laboratory methods in present use have to do with solubility and specific gravity tests. The Bureau of Mines has used ethyl alcohol and claroline oil. One hundred cc. of the gas are shaken with 35 cc. of the oil or with 50 cc. of absolute alcohol until absorption ceases. For the determination of the specific gravity, the gas has been weighed and also tested by Bunsen's effusion method. It was found that gasoline is at present condensed in commercial quantities from natural gases that have a specific gravity of .80 or higher (air = 1), and that are soluble to the extent of 30 or more per cent of their volume in the solvents used. The best way to use the laboratory tests is as a method of testing, preliminary to testing the gas at the well by means of an experimental testing plant.

The pitot tube as ordinarily used for measuring the flow of gases, i. e., where the static pressure is not obtained, may give results that are 8 per cent in error even where the tube is correctly used. When the static pressure is also obtained and all readings are taken with a sufficient degree of refinement, they may only vary 1 per cent from the correct results. Wells should be allowed to vent at least 24 hours before measurements of the flow are made.

A simple gas analysis determination will show an operator whether or not air is leaking into his lines. Some gases that are used for condensing gasoline contain 4 or more per cent of air due to leakage.

Regarding the life of wells as to flow of gas for gasoline condensation, it can be stated that wells from which gas has escaped freely for several years will be long enough lived to insure a return of the initial investment with profit, i. e., if the gas contains in the first place the necessary quantity of gasoline vapors.

The process of the condensation of gasoline from natural gas is a physical one. The process in principal use at the present time consists essentially in compressing the gas up to 300 lbs. per square inch and cooling it with water of ordinary temperature. Cooling the gas by means of a refrigerant (ammonia) at low pressures is a process that is successfully used in at least two plants.

The pressure best suited for the condensation of gasoline from natural gas depends upon the partial pressures of the gases and vapors present in the mixture. These partial pressures are difficult to determine; hence the best one can do in plant operation is

to experiment until the most suitable pressures are found.

Single and two-stage compressors are generally used in gasoline plant operations. Single stage compressors are generally used where pressures up to 110 lbs. per square inch are not exceeded. In two-stage plant operation usually but little condensate is obtained after the first compression.

Several changes occur in the gas when it is treated in a natural gas gasoline plant for the condensation of gasoline. One has to do with the condensation of vapor, another with the liquefaction of gas and a third with the solubility of gases in the liquids produced.

The condensate as it is received in the accumulator tanks consists principally of the liquids pentane, hexane and the liquefied gas butane. Some heptane and liquid propane may also be present.

For the particular natural gas there is a certain pressure which will be found suited to produce the most salable gasoline. Increasing the pressure may result in producing more condensate in the accumulator tanks, but the additional yield may be so volatile as to quickly escape after exposure to the air. The quantity of gas that dissolves in the condensate in the accumulator tank is so small as to be insignificant.

Exclusive of foundations and housing for machinery, pipe lines to wells, railroad sidings, storage tanks, etc., compression and condensing equipment for natural gas gasoline plants costs about \$2,800 for handling 120,000 cu. ft. of gas, and up to \$7,850 for handling 600,000 to 700,000 cu. ft. Two plants that produced 490,000 gals. of gasoline in 1913 cost \$40,000 to completely install. The owners realized 53 per cent on their investment last year.

About 35 cu. ft. of gas disappears at some plants for each gallon of condensate produced from 1,000 cu. ft. of gas.

The heating values of natural gas used for the condensation of gasoline from natural gas may be as high as 2,500 B.t.u. per cubic foot at 0° C. and 760 mm. pressure (gross heating value). None of the residual gases that the authors tested had a heating value lower than 1,000 B.t.u.; at one plant the residual gas had a heating value of almost 2,300 B.t.u.

The explosive limits of natural gases used for the condensation of gasoline from natural gas are very low and very narrow. These limits in some cases are approximately 3.5 per cent gas, low limit, and 8 per cent gas, high limit. Special precautions must be taken to avoid explosions. Some plants have been completely wrecked.

Evaporation losses that resulted when the authors exposed natural gas condensates of different specific gravities to the atmosphere ranged at one plant from 4.5 per cent to 24 per cent at the end of the first hour; from 8.5 per cent to 33 per cent at the end of the second hour; from 9.5 per cent to 40 per cent at the end of the third hour, and about 54 per cent at the end of the 18th and 24th hours.

At another plant the losses of condensates of 79 to 98 specific gravity, Beaume scale, ranged from a trace to 19 per cent for the first hour; from a trace to 26 per cent for 2 hours; from 1 to 34 per cent for 3 hours; from 2 to 38 per cent for 4 hours; from 3 to 45 per cent for 6 hours; from 4 to 48 per cent for 7 hours; from 4 to 46 per cent for 8 hours, and from 10 to 65 per cent for 24 hours.

A slower rate of evaporation occurs from a mixture of refinery naphtha and a condensate than when the condensate is allowed to evaporate separately. In the case of some tests conducted by the bureau the saving at the end of the first hour was about 6 per cent in favor of the blends; at the end of the second hour about 10 per cent; at the end of the third hour about 11 per cent; at the end of the fifth hour about 12 per cent; at the end of the sixth hour about 11 per cent; at the end of the seventh hour about 8 per cent; at the end of the 24th hour about 14 per cent.

Freshly drawn condensates of 93° Be. specific gravity may have a vapor pressure from 14 to 48 lbs. per square inch at temperatures from 55° to 100° F. (13° to 36° C.). Condensates of 78° Be. specific gravity may have vapor pressures ranging from 3 to 19 lbs. per square inch at temperatures from 55° to 109° F. (13° to 43° C.).

After a condensate of 93° Be. specific gravity has lost 40 per cent of its volume by evaporation, the vapor pressures may range from 1 pound to 19 pounds per square inch at temperatures ranging from 55° F. to 109° F. (13° to 43° C.).

When freshly drawn condensates of 93° Be. specific gravity are mixed with refinery naphthas of 60° Be. specific gravity, the vapor pressures may be 57 to 70 per cent of the vapor pressure of the condensate alone.

Condensates of the same specific gravity may have different vapor pressures.

There are shown in Table I the results of analyses of samples of natural gas collected in different parts of the United States. The samples were collected by members of the Bureau of Mines, the U. S. Geological Survey and others.

In columns 1, 2, 3, 4, 5, and 6 are shown the eudiometric analysis. The total paraffins have been calculated to methane and ethane as shown in columns 7 and 8:

Sample No. 1838 was collected in Armstrong County, Pennsylvania, 6 miles from Bradford, from the No. 1 well on the J. S. Somerville farm. The gas comes from the fourth sand.

Sample No. 3177 was collected in Osage County, Oklahoma, in the Hogshooter field. It was taken from the Collinsville pipe line in the pumping station of the Kansas Natural Gas Co., at the north end of the Hogshooter field. This line tapped about 40 gas wells. The initial rock pressure of the well was 490 pounds per square inch. At the date of the collection of the sample (Dec., 1912) the pressure had dropped to 120 lbs. It is a methane gas.

Sample 2121 is a casing head gas from Oklahoma. It was collected on the property of the D. W. Franchot Company, about 2,000 feet east of the railroad station at Kiefer, Okla. It is from the Glenn sand.

Sample 2445 was collected 5 miles from the town of Glasgow, Barren Co., Kentucky, at the Cully well, Ellis farm, of the Oskamp Development Co. The well is 340 feet deep and was drilled in 1903. Hydrogen sulphide was present in the sample.

Sample 2444 was obtained in the same locality as 2445, but from a different well. The latter was 280 feet deep. Both wells were drilled in 1903.

Sample 1031 was collected near the town of Moab, Utah. It is a marsh gas that was bubbling from marshy ground and is different from those gases that are found in the oil fields and which almost always contain appreciable quantities of the higher paraffin hydrocarbons.

Sample 1033 was collected at a nearby seepage in the same locality as 1031. The gas was simply bubbling up through marshy ground.

Sample 1063 was collected from a slough on a farm in Northwest Oregon, Sec. 26, T. 8 N., R. 10 W.

Sample 1893 was collected at Titusville, Crawford Co., Pa., from 15 oil wells, No. 1 to 15 inclusive, of the Atlantic Refining Co. (South Penn. Oil Co.). It is casing head gas.

Sample 1065 is a marsh gas collected in Northwest

Oregon, S. 23, T. S. N., R. 7 W. The gas was bubbling from a spring.

The striking feature of Sample No. 1066 is the high percentage of Nitrogen. This sample was collected 5½ miles southwest of Tillamook, Oregon, Sec. 10, T. 25, R. 9 W. A well had been drilled and this gas was issuing from it in considerable quantity. For present purposes to which natural gas is put, it is of course worthless.

Sample 1378 was collected near the town of Stillwater, Nevada, from a slough about 15 ft. in diameter. This is a marsh gas.

Sample 1871 was collected in Clarion Co., Pa., near the town of Mill Creek. The gas comes from the fourth sand, which is 800 ft. deep. The rock pressure on the well (Sept., 1911) was 300 lbs. per square inch. The capacity of the well was 3,000 cubic feet of gas per day of 24 hours.

Sample 1889 was collected in Forest County, Pa., about 3 miles east of the town of Nebraska. The gas comes from the third sand. Five gas wells were tapped by the pipe line from which the gas sample was drawn. The rock pressure (Sept., 1911) was 62 lbs. per square inch.

Sample No. 1872 was collected in Clarion Co., Pa., near the town of Mill Creek, from well No. 12, of the Mill Creek Gas Co. The gas comes from a different sand (the Bradford or Little Bradford sand) than sample 1871. The sand is 2,100 feet deep. The rock pressure was 850 lbs. per square inch and the capacity of the well 3,000,000 cu. ft. of gas per 24 hours. This gas contains a higher percentage of the heavy paraffin hydrocarbons than does the gas (1871) that comes from the shallower sand.

Sample 1848 was collected at well No. 14 of the A. W. Starr farm (South Penn. Oil Co.) in Butler County, Concord Township, near the town of Chicora, Pa. The gas is from the Speechley sand.

Sample No. 10,000 was collected in the McKittrick Oil fields, Kings Co., California, on the Dabney lease, Sec. 29, T. 20 S., R. 22 E. The high percentage of carbon dioxide will be noted.

Sample No. 3224 is from the Greybull field, Wyoming. It was collected from Island No. 8 well, one of eight that are producing gas commercially. The initial production of this well was 750,000 cu. ft. at a rock pressure of 120 lbs., 1908. In Dec., 1912, the pressure had dropped to 30 lbs. In August, 1912, the combined capacity of the eight producing wells was tested at 1,460,000 cu. ft., but at the end of December, 1912, it was only 800,000 cu. ft. Mr. W. R. Calvert¹ says that the failure to close promptly the first well drilled was highly detrimental to the field, for the amount of gas thus wasted would have supplied the present demand at Greybull and Basin for a period of 24 years. This gas is identical in quality with that used at Pittsburgh, Pa.

TABLE I.—RESULTS OF THE ANALYSES OF SAMPLES OF NATURAL GAS FROM DIFFERENT PARTS OF THE UNITED STATES.

1	2	3	4	5	6	7	8	9	10
No.	CO ₂	O ₂	N ₂	Total Paraf- fins.	Total.	SH ₄	C ₂ H ₆	Gross Heating Value O°C & 760 mm. pressure.	Specific Gravity Air = 1.
1838	.05	.0	1.45	98.5	100.0	81.6	16.9	1184	.64
3177	1.1	.0	4.6	94.3	100.0	94.3	0.0	1004	.58
2121	2.4	.0	1.8	95.8	100.0	64.1	31.7	1272	.74
2245 (a)	2.5	.0	1.3	93.3	100.0	23.6	69.7	1548	.91
2444 (b)	2.6	.0	5.1	92.3	100.0	44.1	48.2	1367	.84
1031	3.6	.0	5.6	90.8	100.0	90.8	0.0	967	.61
1033	3.5	.0	6.5	90.0	100.0	90.0	.0	959	.62
1063	3.0	.0	.9	96.1	100.0	96.1	.0	1023	.58
1893	.0	.0	2.3	97.7	100.0	6.6	91.1	1766	1.01
1065	.5	.0	12.5	87.0	100.0	87.	.0	927	.60
1066	0.1	.0	97.9	2.0	100.0	2.0	.0	21	.96
1378	1.3	.0	3.1	95.6	100.0	95.6	.0	1018	.58
1871	.0	.0	1.1	98.9	100.0	96.4	2.5	1073	.57
1889	.0	.0	1.0	99.0	100.0	70.8	28.2	1279	.70
1872	.0	.0	1.7	98.3	100.0	80.5	17.8	1189	.65
1848	.6	.0	.9	99.1	100.0	53.3	45.8	1120	.78
10000	30.4	.0	2.4	67.2	100.0	66.2	1.0	724	.85
3224	.2	.0	.8	99.0	100.0	81.70	17.3	1192	.64
3222	.0	.0	1.3	98.7	100.0	51.5	47.2	1127	.77
3220	.5	.0	3.1	96.4	100.0	64.1	32.3	1282	.68
4829	.0	.0	1.	99.0	100.0	86.0	13.0	1159	.59
4759	.9	.0	1.5	97.6	100.0	97.6	.0	1039	.57
4416	.0	.0	1.8	98.2	100.0	94.1	3.8	1076	.59
4444	.0	.0	8.9	91.1	100.0	18.90	72.2	1534	1.00
4057	1.3	.0	13.6	85.1	100.0	85.1	.0	907	.62
3181	.5	.0	1.5	98.0	100.0	76.4	21.6	1215	.67
*A	.0	.0	3.3	96.7	100.0	...	18.0	2424	1.38
B	.0	.0	1.2	98.8	100.0	79.2	19.6	1208	.65
C	.0	.0	1.6	98.4	100.0	80.3	18.1	1193	.61

(a) H₂S=29%.

(b) H₂S=1%.

* C. H₄, 78.7.

¹Calvert, W. R., "A Preliminary Report on the Utilization of Petroleum and Natural Gas in Wyoming." Technical paper 57, 1913, Bureau of Mines.

Sample No. 3222 is a casing head gas from a well in which some oil is found.

Sample 4829 was collected in the Mt. Jewett field, McKean County, Pa. The St. Marys Gas Co. own the well. The total number of wells in the district is 69. The initial rock pressure on the well in the year 1900 was 600 lbs.; at the present time (1914) it is 300 lbs.

Sample 4759 is from the town supply of Little Rock, Ark. The gas comes from the Caddo Parish field, Louisiana, 165 miles away. It is a methane gas. Sample 4446 was collected in the town of Cody, Okla., Park County. The Enalpac Oil & Gas Co. operate the wells.

Sample 4444 was collected in the town of Bradford, Pa. The gas is casing-head gas from oil wells.

Sample 4057 was collected in Kennison Township, near the town of Mortonville, N. D., Sec. 20, T. 136, R. 64.

Sample 3181 was collected in the Schuler field, Okla. The initial production of the well was 22,000,000 cu. ft. per day. In Dec., 1912, the production was 6,000,000 cu. ft. Mr. R. S. Blatchley, Consulting Geologist to the Bureau, who collected the sample, states that there has been 1,776,000,000 cu. ft. of gas wasted from the well.

Sample A is a casing head gas used for the production of gasoline. The gas is drawn from 49 oil wells at Riverside, W. Va., and is compressed to 90 lbs. per square inch and cooled. The high heating value will be noted.

Sample B is from the Pittsburgh Natural Gas Supply. The gas varies slightly in composition at different times, although not enough to be of consequence.

Sample C is from the Columbus Natural Gas supply. It is practically identical with Pittsburgh gas. These gases are typical of that supplied to many towns in Ohio, West Virginia and Pennsylvania.

The foregoing analyses are given to show how natural gases vary in composition at different places. Those given are marsh gases, containing only methane as the combustible constituent, casing head gases in which the higher paraffins predominate and gases that are used for heating and lighting large cities like Pittsburgh and Columbus, and which contain methane as the predominating paraffin, but also small quantities of the higher paraffins.

One gas of exceptionally high nitrogen content is shown (98 per cent) and another with 30.4 per cent of carbon dioxide.

The marsh gases are not the factor in the uses to which natural gases are put, that other gases mentioned are. Occasionally a deposit is found sufficient for small local use and in some of the oil fields immense deposits exist, but they are small compared to the great volume of gas that is used, that contains other paraffins in addition to methane.

Casing head gases are largely used on oil leases for driving pumps and lighting and heating buildings. In some cases they are turned into mains and sent to cities. Their most important use is for gasoline extraction. When the supply on the lease exceeds the local demands or is unsuited for gasoline extraction, it is wasted. Far more is wasted at the present time than is used. Many miles of pipe lines would have to be installed to gather it all and transport it for city and factory use, even if the market was available. In many cases the expense would be unwarranted. However, some small towns are largely heated and lighted with casing head gas.

By far the largest quantity of natural gas used contains methane as the predominating constituent with smaller quantities of the higher paraffins. That used in Pittsburgh contains about 85 per cent methane as shown by fractionation analyses. Most of that obtained from West Virginia and distributed to neighboring states is similar in composition. That used in Pittsburgh has remained of remarkably uniform composition during the four years the bureau has tested it. It has been suggested that natural gases be sold on a heat unit basis. In the case of Pittsburgh gas nothing would have been gained from such procedure during the four years mentioned, because the gas has not fluctuated in composition enough to warrant it. Presumably this applies to other places that derive their gas supply from the same source. A complete series of analyses would have to be obtained from many localities in order to determine whether such a procedure would be warranted in other places.

It is believed, however, that natural gas companies themselves would derive benefit by making analyses of the gases from different wells on their properties. Some high nitrogen gases have been found in Kansas for instance. It might be that an occasional well would be found producing a gas of abnormally low heating value. Probably not enough to appreciably affect the average output of the field but of enough importance for the gas company to know it. The Bureau of Mines is making such a survey of several fields.

INCREASE IN SULPHURIC ACID OUTPUT.

According to actual returns made to the United States Geological Survey the production of sulphuric acid in the United States in 1913 was 3,538,980 short tons of 50° acid, valued at \$22,366,482. This output does not include a small amount of fuming acid, but does include by-product acid—that is, acid obtained in the smelter industry. The acid produced at copper and zinc smelters in 1913 amounted to 790,296 short tons of 50° acid, valued at \$4,346,272. The year 1913 is the third for which statistics of sulphuric acid have been collected by the Geological Survey. The 1913 output of 50° sulphuric acid was 662,980 short tons greater than that of 1912.

VALUES FROM CITY GARBAGE.*

In the disposal of city garbage incineration has obtained a considerable following among smaller municipalities on account of its so-called sanitary features, in that the material used is entirely destroyed and there remains no offensive clinker. This, however, is scarcely warranted by the fact. The method of incineration involves the collection of garbage in the usual manner and depositing same at the incinerator plant in heaps or in bins which are very difficult to keep in a cleanly condition. The furnace is itself free from objection. It is very difficult, however, to prevent the diffusion of very offensive odors polluting the atmosphere for miles around the incinerator during the process of incineration. So far as the disposal of garbage is concerned in incinerators, it is coming to be generally understood that the method is far from sanitary and is essentially wrong in that it neglects to obtain the value from the products so collected. As an index of the importance which the incinerator method has obtained in this country, it might be well to state that during the year 1909 a little more than 12½ per cent of the total amount of garbage reported in the cities of more than 30,000 population was destroyed in this manner.

The reduction system is, in the eyes of the American public today, by far the most prominent method of disposal, and, judging from the volume being handled by that method, outweighs all others combined, there being more than 60 per cent of the total garbage collected in 1909 treated in that manner. The importance of this method of treatment becomes apparent to all students of the subject. Many objections have been raised to the reduction system on account of some instances where it was attended with unsanitary surroundings. There is, however, no reason why the reduction system need not be the most sanitary method of disposal and at the same time the only method which conserves to the fullest extent the values contained in the refuse. The reduction system itself is susceptible of so many variations in treatment that it will require a subdivision into different methods in order to thoroughly understand the manner in which materials are being treated for the recovering of waste throughout the length and breadth of this country. The system essentially consists of the reduction by the application of heat to the materials, producing an innoxious tankage and certain recoverable products more specifically described hereinafter. The method of obtaining the different values varies and may be outlined as follows:

Direct drying.

Digesting, or cooking.

In the direct drying system the material is fed directly into a revolving cylindrical shell through which are also carried the products of combustion

from the furnace of the dryer. The water which is present with the garbage is, of course, driven off under this process and the material is subjected to sufficient heat to thoroughly sterilize the product. This method does not permit the recovery of any considerable portion of grease, but does provide for the retaining of most of the solids in dried form, after which they may be ground up to serve as a base for fertilizer. A large percentage of the ammonia, however, is driven off in the process of drying and a considerable portion of the solid matter is charred or destroyed by contact with the tremendous heat which is necessary for the proper pursuance of this method. The material may be handled very promptly in this manner and the dried tankage resulting after grinding contains some value as fertilizer, but does not contain nearly the full percentage of grease that was in the original garbage, on account of the charring action in the dryer.

The direct heat system is open to some objection on account of the escaping gases from the stack of the dryer; that is, unless efficient scrubbers intervene between the dryer and the stack there are likely to be odors which are very offensive and very similar to those produced in the incinerator method, described above.

The digesting system consists essentially of placing the raw garbage in closed steel tanks having capacities ranging from one to ten tons each and cooking therein by the aid of steam for a period of from four to eight hours. It is usual to maintain approximately 70 lbs. steam pressure in the cooking chamber or a little higher, which temperature is sufficient, from a bacteriological standpoint, to reduce the danger from spread of disease to a minimum and to render the product entirely sterile.

At the conclusion of the cooking process, it is usual to draw off the liquids, which consist of the condensed steam and grease resulting from the breaking down of the fibrous product in the cooking process, and to separate the grease from the water by some method of flotation. Under the most modern methods, also, the water itself is taken to a close receptacle and afterwards fed to an evaporator where the values contained therein are recovered by an evaporation of the surplus water. The fibrous material, after cooking, is removed from the condensers and taken to some form of dryer where the surplus moisture is driven off, after which the product is passed to a percolating plant where the remainder of the grease is extracted by continued washing with some form of grease solvent, usually naphtha or benzol of some kind. The solvent is separated from the grease by means of the application of heat and the use of a condenser which aids in the distilling of the solvent and the consequent separation of the grease.

This system of percolation may also be used in connection with the direct system, and in this way a large portion of the grease can be recovered. As this

*From a paper by C. O. Bartlett, presented before the Cleveland Engineering Society.

grease has absolutely no fertilizing value, it is important to retain it as grease. The tankage contains the fertilizing elements and should, therefore, be returned to the land. The solid matter which is obtained by drying the water from the process of cooking should also be returned to the tankage. This product is technically known as "stick" and contains most of the ammonia and practically all of the glues which were in the original garbage as delivered to the plant.

The cost of treating garbage by the reduction system varies from \$2 to \$2.50 per ton of raw garbage delivered to the plant.

According to the report contained in the *Municipal Journal*, there were burned about 535,000 tons of garbage during the year 1912. Had this garbage been properly saved, it would have produced more than 75,000 tons of the finest kind of fertilizer, and it would have produced 21,000 tons of grease worth at the present time \$1,890,000.

To further illustrate, San Francisco burns about 150 tons of garbage a day. California produces a large amount of citrons fruits and other agricultural products, and in order to do so purchases a large amount of commercial fertilizer which is daily manufactured in Chicago, and shipped from Chicago to the coast and sold at a profit, this fertilizer largely composed of the identical material that San Francisco has burned.

To still further illustrate the importance of this matter, during 1912 we imported 486,000 tons of nitrate from Chile. This is worth \$44 a ton in New York. We imported 890,000 tons of potash salts from Germany, worth about \$54 a ton in New York. There is no other place from which to get the above materials, which are absolutely necessary to supply the commercial fertilizer used in the United States.

Cleveland has one of the best garbage plants in the United States, and considering the amount of capital invested in its buildings, it is not only the best, but the best managed one. In 1912 the Cleveland plant produced 2,940,000 lbs. of grease and 10,016,000 lbs. of tankage and received from same \$151,162.48. The reduction cost per ton of green garbage was \$1.97½, and the earnings per ton of green garbage was \$3.47. Net earnings per ton of green garbage was \$1.49½.

FEED WATER DIFFICULTIES.

The problem of suitable feed water, although less serious in New England than in other parts of the country, is still a trouble maker in many plants. The formation of scale and the softening of water are due to the simplest of chemical reactions, and by an analysis of the water a competent chemist can readily predict in advance the proper amounts of suitable chemicals necessary to prevent scale or corrosion, and not only save the company the expense of frequent boring and replacing of tubes but obviate the necessity of attempting to force heat through the same substance with which many of your steam lines are in-

sulated. "The services of a chemist," said Mr. Carl F. Woods, secretary of the firm of Arthur D. Little, Inc., of Boston, when recently speaking before a group of street railway operators, "would prevent the purchase of a special compound at \$1,000 a year which consisted of 97 per cent water and 3 per cent molasses, or obviate the necessity of purchasing a mixture of soda ash, tannin and water under a brand name at 8 cts. a pound when the principal ingredient can be obtained for 1 ct. a pound."

GERMAN DETINNING METHODS.

The recovery of tin from tin-plate waste has recently gained great importance. There are three general methods of separation—mechanical, chemical, and electrolytic. Blücher states that in the mechanical process, which incidentally has produced only poor results, the tin is melted or thrown off during heating.

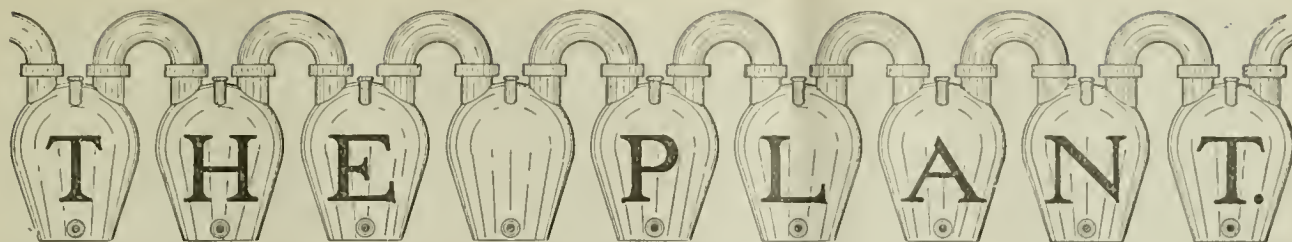
In chemical separation, the tin-plate waste is treated at a low temperature with diluted hydrochloric acid, nitric acid, or sulphuric acid solutions and the dissolved tin drops out with the zinc. Other dissolving agencies have been experimented on with varying success.

Much more important than either the mechanical or the chemical process is the electrolytic method of detinning. As a rule, hot caustic soda (liquid) is employed as electrolyte (6 to 7 per cent Na_2O). Loosened chips of tin plate packed in wire baskets act as anodes while the iron bath walls or iron plates suspended therein serve as cathodes. The average tension is said to be 1.5 volts. When separated, the tin is spongiform.

In other processes acid electrolytes are employed. Thus in the older Siemens & Halske process chips of tin plate packed in wood-latticed baskets serve as anodes, the cathodes consisting of tinned copper. The electrolyte is made up of a solution of 1 volume of 60 per cent sulphuric acid and 9 volumes of water. The density of the current is about 100 amperes to the square meter (10.764 square feet).

Recently Siemens & Halske have also been employing an alkaline electrolyte that offers great advantages over the acid electrolytes formerly used. At any rate, it may be safely stated that the electrolytic methods utilizing acid and ferrosulphate electrolytes have not been shown to possess any practical value.

By far the greatest amount of tin-plate waste is now being detinned by the chloride method that Lambotte, of Brussels, was the first to apply on a large scale. (Imperial German letters patent No. 32,517.) The principal requirements for a successful application of this method are absolute exclusion of moisture during the process of detinning, avoidance of an unduly high temperature, and proper washing of the detinned waste. The process is protected by Imperial German letters patent Nos. 176,457, 176,456, and 188,018.



TECHNOLOGY OF THE SULPHITE PULP PROCESS.*

In a comprehensive account of the sulphite pulp industry contributed to the *Pulp and Paper Magazine*, G. B. Steffanson describes the woods used and their treatment. He prefaces the article with an historical review of inventions, beginning with that of Tilghmann in 1866. Much of the introductory matter is commonplace, but necessary to complete the record. Speaking from the Canadian standpoint, he says of the woods used:

On this continent the kinds of woods used in sulphite pulp manufacture are principally white spruce (*Picea alba*), black spruce (*Picea nigra*), balsam fir (*Abies balsamica*), hemlock (*Tsuga canadensis*), to some extent tamarack or larch (*Larix americana*) which is, however, nearly extinct, and in the Western States the cotton wood (*Populus deltoides*).

Aspen (*Populus tremuloides*) and poplar (*Populus alba*) have to some extent been used in sulphite pulp manufacture in Europe, but the match factories are now buying this wood at prices which are much higher than the price of other kinds of pulpwood. On this continent these woods are only used in isolated cases for the manufacture of sulphite pulps.

In order to obtain a uniform pulp, it is of great importance that different kinds of wood are not cooked in admixture, as the different incrustations require varying lengths of time for their decomposition. Even the same kind of wood cut on different grounds may produce irregularities in the pulp if cooked together.

White spruce yields a white free rosin, but not so very strong.

Black spruce is more resinous and some care is required in the manufacture, but the pulp is stronger than that produced from any other kind of wood on this continent.

Balsam fir contains a large proportion of rosin and care must be taken to remove it in the manufacture. The pulp is of good color but not strong.

Hemlock gives a somewhat coarse dark pulp which is free from rosin and is quite suitable for newsprint and similar papers where a high color is not essential.

Tamarack is resinous but gives a fairly high colored pulp. The fiber is shorter than that of spruce.

The Scandinavian spruce (*Pinus sylvestris*) yields undoubtedly the strongest fibers of all kinds of wood used in the manufacture of sulphite pulp, but if prop-

erly cooked, both white and black spruce should yield a pulp that in strength could compete with the majority of Scandinavian and German brands of sulphite pulp sold in this continent.

For the production of bleached pulp the wood in this country should be more suitable, because it does not as a rule contain black knots which cause endless trouble in some parts of northern Europe.

THE TREATMENT AND TRANSPORTATION OF WOOD.

The wood should preferably be cut between the middle of November and the middle of March, as wood cut during this period gives the strongest fiber and does not rot very easily.

If the wood is to be dried before it is taken out of the bush, and the place where it is piled or left to dry is not open and windy, the bark should be stripped off the log in strips a few inches apart to admit the air to the wood in order to prevent rotting and the growth of fungi.

The wood which is to be peeled should be cut as early as possible while the sap runs as the fiber loses in strength while the sap is running. The bark should be peeled off, and the branches removed only so far as the tree is meant to be cut up for pulpwood, the top being left intact, the tree being left in this condition for about six weeks before it is finally cut up. While the tree lies thus, the bark, branches and the needles in the top attract the sap, which causes the wood to contract, so that later no cracks are formed in drying, which absorbs dirt, specially in driving in the rivers.

In any case the branches should be carefully removed, large knots take up a lot of room in racking the wood, and cause inaccuracy in measuring and great trouble where the wood has to be rossed. This applies particularly to wood of small dimensions.

The transport of the wood in the forest, in the river, or by rail need not be discussed here, as it is the business of the wood ranger.

The arrangements for the transportation of the wood from the boom or railroad car to the wood room or the pile may be arranged in many different ways. The problem before the engineer is to construct the most economical transportation arrangements, with due regard to location, wages, cost of materials, the demand for uniformly dried wood, etc. The old method of conveying the long logs from the boom or car, by means of an elevated conveyor, to large storage grounds where it is piled in such a manner as to allow the air free access, has many ad-

*From Paper.

vantages, particularly if high grade pulp is manufactured. The wood is in this case usually taken to the wood room on railway cars.

This system is still very extensively used in European mills, but it can only under certain conditions be considered suitable in Canada, on account of the higher wages.

It is more economical to take the wood to the slashers first by means of chain conveyors and further to the pile or mill on chair conveyors or water spouts. These conveyors should be so arranged that one high conveyor takes the wood to the piles, and the returning chain, under the pile, takes it to the mill, or so that one conveyor takes the wood to the high conveyor at the pile as well as to the conveyor connecting the pile with the mill.

A suitable form of conveyor in the wood room is a wide water spout running alongside the barkers and provided with a circulating pump. In cold weather the water in this spout should be warmed so that the wood is thawed out before reaching the barkers.

PREPARATION OF THE WOOD.

There are three types of crosscut saws, the balance saw, stationary circular saw, and the band saw.

The balance saw is cheap but has a small capacity, and is out of question except in small mills.

Stationary circular saws, so arranged that the logs, by means of chains, are carried over a table provided with a number of saws, are cheap in first cost and maintenance; all types of circular saws, however, cause a considerable loss of wood, particularly if the wood is of large diameter, when the thickness of the saw requires increasing.

The band saws are also provided with chains which take the logs to and past the saws. Both the ascending and the descending portion of the saw blade do the cutting, and the length of the cut logs is equal to the diameter of the saw pulleys. This type of saw is the most expensive one, but for large mills it is economical because it causes less loss through sawdust than circular saws.

Disregarding hand barking, there are three methods of barking done by different types of machines—namely, the drum barkers, the automatic barkers for long logs and the disk barkers.

The drum barker is the most economical of all barkers, although it is much more expensive than other barkers and requires about 50 per cent more power. It saves all the wood wasted by other machines, which amounts to from 6 to 16 per cent or even more. The drum barker is, however, suitable only in sulphite mills where clean pulp is not very essential, or where bleached pulp is manufactured and the look of the unbleached pulp is of no consequence. The drum barkers do not remove all the last thin layer of the bark, and it would be too costly to remove it by hand. This thin layer of bark retains a dark color after cooking, and shows up as dark fibers or dirt in the pulp which is, however, quite as easily bleached as

any other part of the pulp. It is to be noted that the water in the drums has to be heated, and this causes extra expense, unless some exhaust steam, which otherwise would be wasted, can be used for the purpose. The attendants required for drum barkers in a large or medium-sized mill are less than for other barkers, but as any bark remaining in cracks or round knots must be removed by hand, or for some drum barkers part of the wood sent through twice, the saving in wages is not very large.

Automatic barkers are most suitable for wood of small dimensions, but much attention is necessary, and reliable men should work the machines to keep down the loss of wood. It may be remarked here that these machines are usually built for the barking of logs before they are cut up into lengths fit to handle.

The most common barking machines are the disk barkers of which there are several types. The usual type with four radial knives waste a considerable proportion of good wood, because the operator turns the log by hand, and when he changes the position of his hands the knives cut over a portion of the log which has already been barked. Wood which has been barked on such a machine is easily recognized by the angular surface which it presents.

In order to prevent this waste, barking attachments have been designed. They bark the wood more uniformly, but in order to give the machine capacity, the knives must be set to project 1-16 in. or more, which also causes great loss of wood.

Undoubtedly the most economical disk barker is the machine which was introduced in most of the Scandinavian mills about fifteen years ago. In this machine the knives are parallel with the diameter of the disk and not radial. The wood is supported on adjustable blunt-edged supports placed at right angles to the disk, and to prevent a longitudinal motion of the log, one end of it rests against a swivel point or a ball. The knives touch the log tangentially and cause it to rotate. All the operator has to do is to keep the log against the disk and prevent it from rotating too fast. These machines have a greater capacity than any other type of disk barking machines, as no time is wasted in turning the logs or manipulation of barking attachments. The knives need not and should not project more than 1-32 in., in order to save wood.

In barking wood with all the bark on, the losses in using the different machines are approximately as follows:

Drum barkers 10 per cent.

Automatic barkers 15 to 35 per cent.

Disk barkers with attachment and radial knives 20 to 30 per cent.

Disk barkers with knives parallel to the diameter of the disk 15 to 20 per cent.

The bark is about 9 per cent of the total wood, the remainder being loss of useful wood. In barking wood which has lost the greatest part of the bark in driving the loss of wood is higher.

In a well arranged wood room, the logs should be conveyed as close to the barker as possible, so that the operator can easily reach them, and there should always be an ample supply of wood at hand. Cross conveyors operated by the barker man are apt to cause considerable waste of time.

The conveyors from the barkers to the chippers should be arranged so that the logs need not be lifted from the barkers but can be allowed to slide on to the conveyor. If possible these conveyors should be arranged on the floor below the barkers and they should be of the chain or belt type, and feed the wood into the chipper spout, so that the chipper man can give most of his attention to the chipper, which is of great importance.

The barking machines should be provided with fans, cast in one piece with the disk for blowing the bark into the boiler house, or to a waste conveyor. The machines should be able to blow the bark to cyclone separators in the boiler house, unless the distance is greater than about 600 feet, provided there are no sharp turns in the pipes. In case of greater distance, a covered conveyor into which the bark is blown must be used. All the bends in the pipes should be of as big radius as possible, and the bark should be blown into the conveyor, in a direction coinciding, as nearly as possible, with the direction of motion of the conveyor.

The barkers should be driven individually, either by motors or from countershafts. In the latter case the countershaft should have a tight and a loose pulley against the main shaft, so that any one machine may be stopped without stopping them all, and without having the barker belt running during knife changing. In a large mill this arrangement saves time, and one man can be made responsible for the correct setting for all the knives. When the barkers work on individual piece work, this arrangement is particularly satisfactory, especially when all the barkers take their wood from the same conveyor. The knife grinder then changes the knives in all the barkers in turn at fixed intervals, and the men moved from one machine to another are thus all supplied with wood at the same rate.

The disk chipper is now used almost exclusively. In a few old mills in Germany circular saws are still employed, but the guillotine chipper is no longer used. There are a few different types of disk chippers. The number of knives is usually two or three, arranged radially. The spout may be parallel to the shaft and inclined against the disk, or inclined against both the shafts and the disk. The disks are made either of cast iron or cast steel. Of these the more expensive machines with cast steel disks, two radial knives, and a spout inclined against the disk and the shaft are preferable. Cast steel disks do not crack as easily as cast iron disks do, thereby risk of life and stoppage is diminished. The inclined spout makes for economy of

power, as the plane of the cut is at a more acute angle to the fiber in the wood.

Two knives have been found to be quite sufficient in most cases. The knives should be set to work as nearly parallel to the plane of the cut as possible. By this means the chips are broken up better, which is of special importance where no disintegrators are employed. Frequently, chippers with a fan combined are employed, and in such cases the chips are blown to the disintegrators or chip screens. The cost of maintenance of such chipper arrangements is low, but they require more power than other chippers.

It is bad policy to judge a chipper by its capacity alone, because if the chipper is heavy enough there is practically no limit to its output, but the quality of the chips suffers accordingly. The speed of a chipper should never be greater than to allow the logs to fall against the disk between the cuts. In case of higher speed the losses through "sawdust" are considerable, and the chips become uneven.

Unless the chipperman's time is occupied with carrying wood, he has plenty of time to see that the logs enter the spout properly, and to keep them from jumping in the spout, which causes uneven chips and the production of a great quantity of long slivers and sawdust. In cold weather the logs should be properly thawed before going into the chipper, in order to obtain uniform chips. For this purpose a thawing tank should be arranged, preferably in connection with the above-mentioned water spout conveyor.

The working of the chipper can be judged, apart from the appearance of the chips, from the amount of sawdust obtained from the fine chip screens. This should not exceed 3 per cent.

Another important factor in obtaining uniform chips is the condition of the bed knives in the spouts which should never be blunt. This point is very often neglected, particularly in old mills where the chippers are of such a design that the changing of these knives is a lengthy and expensive proceeding. This is, however, easily remedied by fitting the machine with a modern spout, as supplied with up-to-date chippers, where the bed knives can be taken out and regulated from the back side of the spout.

The chipper should stand on a perfectly rigid foundation, but the bed plate of the machine should rest on a layer of hard, tough wood, or specially prepared liner felt. This is necessary in order to diminish the vibration, and modifies the risk of bursting of the disk, and generally prolongs the life of the machine.

Where cast iron disks are employed, it is advisable to carefully shrink stout steel rings on the circumference of the disk, in order to prevent it from bursting completely in case it should crack, which happens frequently on account of the uneven heating they are subject to.

There are four distinct types of disintegrators: the coffee mill type, Can's disintegrator, the Lombard type and the tooth crusher type.

The first type is very similar to the old coffee mill. It requires little power and is the only adjustable disintegrator, but its capacity is comparatively small, and it requires more space and is more costly to install than the other types.

Can's disintegrator consists of two or more disks on a horizontal shaft running inside a housing. The disks are provided with two or more rows of pins fastened to their sides, and these pins run between rows of pins fastened to the housing. The other end of the pins should be joined by steel rings, to prevent them from bending, unless the whole machine is made of cast steel. This disintegrator is most commonly used; it requires more power than other types, but it is cheaper at first cost and up-keep. The machine should be placed on a firm but tough foundation.

Lombard's disintegrator is similar in construction to Can's but the chips are broken up by means of movable arms. This machine requires somewhat less power than Can's but is less effective. The first cost of a Lombard machine is considerable and it is expensive in up-keep.

The tooth-crusher is of a later design. This disintegrator seems to find a growing market on this continent.

All the disintegrators reduce more or less of the chips to sawdust, but where the chips are to be screened on coarse screens they can not be dispensed with, unless the chippers break up the chips thoroughly. Where it can be arranged the disintegrator should deliver direct into the chip screen, in order to avoid using a conveyor.

There are two types of chip screens—flat shaking screens and rotary screens. Where the screens can be arranged on a solid foundation, the cheaper flat screens are to be preferred. If the screens have to be arranged on a top floor, or on wood structures, rotary screens are the better type.

The flat screen should be inclined about 10° and they are usually made double, the top one being coarse, and the lower one a fine screen. Conveyors are arranged to remove sticks and knots, sawdust and chips, to the rechipper, boiler house, and chip bins respectively.

The cheapest screen plates as regards upkeep are perforated sheet steel plates, but they have a much smaller capacity than wire screens. For longer chips ($1\frac{1}{4}$ in. and longer) a wire screen with rectangular meshes is preferable for coarse screening. A suitable wire for this purpose is made with $\frac{1}{4}$ or $\frac{3}{16}$ in. wire for warp, and $\frac{3}{32}$ in. for weft. The weft is wound round the warp for a distance equal to the width of the meshes. The warp wires are 6 to 7 in. apart, and the distance between the wefts varies with the chips from $\frac{1}{4}$ to 1 in. The holes in the perforated plate should be of a diameter $\frac{3}{8}$ to $\frac{1}{2}$ in. larger than the length of the chips. The fine screens should have perforations not larger than $\frac{3}{4}$ to $\frac{7}{16}$ in. in diameter. Ordinary steel wire, with $\frac{1}{4}$ in. mesh is suitable for

fine screens, and inexpensive, although it has to be changed frequently.

A good way of utilizing the screenings is to arrange two fine screens, one with not over $\frac{1}{4}$ in. mesh, and the second with $\frac{1}{2}$ in. mesh. The fine sawdust is burned, but the coarser sawdust, mostly consisting of chips broken too much by the disintegrator, is collected in separate bins and cooked separately. These fine chips take more space, so that the output of the digesters will be diminished, but they can be cooked with weaker acids and give a very clean pulp.

The rotary chip screens can be arranged consecutively in one length supported on rollers. It is, however, cheaper in upkeep to arrange them separately in steps, and with throughgoing shafts, although they occupy a larger space when arranged in this manner.

There are many types of rechippers, of which a miniature wood chipper is the best from many points of view. They all produce an inferior quality of chips, however, and the sticks and knots would probably be burned to better advantage, especially in Canada where wood is generally cheap and coal is expensive.

The chips should be taken to the bins by means of bucket conveyors instead of fans. The latter produce large quantities of dust or wood-flour, which in cooking consumes acid without yielding any pulp, and sometimes this dust appears in the pulp, uncooked, in the form of specks.

The lengths of the chips depends on the method of cooking employed. For Mitscherlich unbleachable pulp, the chips should be $1\frac{1}{4}$ to $1\frac{3}{4}$ ins.; for ordinary newsprint or "quickly coked" pulp, $\frac{3}{4}$ to 1 in., and for unbleachable pulp $\frac{5}{8}$ to $\frac{3}{4}$ in. long.

In many mills the cost of the preparation of the wood is kept down to such an extent that the quality of the chips suffer considerably, quite regardless of the fact that much more can be gained by less waste in the wood room, not to speak of the better price obtained for cleaner pulp. The greatest part of the dirt in the pulp is undoubtedly due to the faulty treatment of the wood, not only in the barking, but still more in the chipping and screening.

In preparing the wood the production of uniform chips, both as regards size, and their being free from dust, large sticks and knots, is of the greatest importance. The pulp produced from uniform clean chips is strong, uniform and clean. Slivers and dirt once in the pulp are very difficult to remove completely.

The yield from uniform chips is much greater.

Where different kinds of wood are used, it is of great importance to cook them separately. The incrustations in the different kinds of woods are not very different, as far as modern research work has shown, but they are present in different quantities, and react with varying rapidity with the acid. In several European mills, wood from trees of the same kind grown on a rocky, and on a fertile soil are cooked separately, in order to avoid an uneven pulp,

but this is of little or no importance when the wood is not properly seasoned, and thus shows varying absorption of acid.

The amount of wood used per ton of pulp produced varies considerably, and this factor of the manufacture is often capable of being considerably improved. Many mills used as much as 2, or even $2\frac{1}{4}$ cords of wood per ton of pulp.

With medium quality of rough seasoned wood, the quantity required for strong Mitscherlich pulp, should not exceed 1.65 to 1.70 cords; for ordinary "quickly cooked" pulp, 1.80 cords; and for bleachable pulp, 1.9 cords per ton of 2,000 lb. It is to be noted, however, that the better utilization of the wood means, as a rule a slightly increased cost of labor. In many cases the increased yield of pulp is worth many times the increased cost of manufacture, but often the installation of the most suitable machines, and the proper supervision of the wood room, wipes out any difference in the cost of preparing the wood, and sometimes even lowers this cost.

It is hardly possible without going into many details to give figures of the capacity of the different wood preparing machines. An idea of how far the different types of machines may be forced economically, is given here on the assumption that the wood comes to the mill in lengths of 20 feet, or in shorter lengths divisible into lengths of $2\frac{1}{2}$ ft. and that the wood is cut up into lengths of $2\frac{1}{2}$ ft. and is of medium size and quality, with regard to straightness, knots, etc.

A balance saw can cut six cords per hour while stationary circular saws and band saws will handle as much as fifty cords an hour.

The drum barker cleans about one cord per hour. The capacity of automatic barkers depends entirely on the speed with which they are fed, and the barking arrangement, but generally speaking they have no greater capacity than an ordinary disk barker.

A disk barker with radial knives, and fitted with a barking attachment, should have a capacity of from 1.2 to 1.4 cords per hour, and a disk barker with the knives parallel to the diameter, should have a capacity of 1.5 to 1.7 cords per hour.

A chipper with two knives, making long chips, should run 175 to 200 r.p.m., and 225 r.p.m. for shorter chips.

If the chips should be uneven in spite of the machine being properly fed, the speed must be decreased until the desired result is obtained.

There are chippers on the market guaranteed to cut fifteen cords per hour, but it is not advisable to calculate for more than ten cords per hour, even with the largest machines, if uniform chips are desired.

The capacity of the disintegrators depends on the length of the chips and the size of the machine. It is advisable to have one disintegrator for each chipper. Coffee mill type disintegrators of a sufficient capacity for large chippers are, however, hardly to be found.

When different lengths of chips, or different kinds of wood are chipped, the speed of the disintegrator should be variable, except in the case of the coffee mill disintegrator which can be otherwise adjusted.

The capacity of chip screens is usually taken to be 1-10 of a cord per square ft. per hour, but this capacity can be very much exceeded, although the quality of the chips suffers accordingly.

Rotary screens have a somewhat larger output per square foot than shaking screens.

The best arrangement is to have one chip screen for each chipper.

PREPARATION OF THE ACID.

The acid used is the aqueous solution of calcium or magnesium bisulphite, containing a large portion of free sulphur dioxide. $[(CaMg)(HSO_3)_2 + 2H_2SO_3 + H_2O.]$

It is prepared from sulphur (S) or iron pyrites (FeS_2), and limestone or dolomite ($CaCO_3$ or $MgCO_3$) or burned lime or magnesia (CaO or MgO).

The acid making comprises four different operations—viz.: the burning of the sulphur or pyrite for obtaining the sulphur dioxide (SO_2), the charging of the limestone or the slaking of the quicklime, the acid making proper by combining the two products and water, and the recovery of the SO_2 which last operation is intimately connected with the cooking.

The acid making plant consists of the following parts: Sulphur or pyrite burners, gas washers and coolers, the acid making apparatus, coolers for recovered gas, and storage tanks.

There are two main types of sulphur burners, the old retort, and the newer rotary burner. The retort can be used with advantage when pure sulphur (99 per cent or more) is burned, especially if Silician sulphur is used and the retorts are fitted with melting pots for sulphur on top, from which the sulphur runs down. This is done in order to prevent an excess of air in the retort, and in order to dry the sulphur.

It is very important that the admission of air into the burner can be regulated accurately, and that hot secondary air can be admitted in such a manner that it is thoroughly mixed with the gas from the burner, in the combustion chamber, at the back of the burner.

The rotary sulphur burners can be used to advantage for burning impure sulphur, or sulphur liable to form an oil skin on the top of the melted mass. The impure sulphur should, however, be avoided, unless it can be obtained at a very low price per unit of pure sulphur. When burning low grade material, the burners have to be frequently cleaned, and this causes interruptions and increased cost of working them.

The rotary burners cannot conveniently be fitted with melting pot, but there are other kinds of automatic feeds. Attention should be paid to the proper regulation and admission of air, and hot secondary air as mentioned above.

The old type of pyrite burners with movable grates has now gone out of existence almost completely, part-

ly on account of the high cost of working these burners, and partly because of the waste of materials in crushing the pyrite to suitable size; the main difficulty with this burner is that the cinders still contain about 4 per cent or more of sulphur, which makes them unfit for iron manufacture.

The most commonly used pyrite burner is the Herreshoff burner, which is a cylindrical vertical shelf burner, made of acid proof and fireproof brick with a sheet iron shell. There are usually five shelves in the burner, and arms, and carried by a vertical air-cooled shaft, rake the materials from one shelf to the next one.

A dryer made of sheet iron of the same construction as the shelves in the burner, and forming the top of the burner, should be fitted in order to prevent the pyrite entering the burner in a moist state. Otherwise wasted hot air from the burner is used for this purpose.

The pyrite should be fed automatically to the dryer and from there into another adjustable automatic feed arrangement on the burner.

When starting up the burner has to be heated by means of coal or wood, and the pyrite fed into the burner. The burners should be fed at such a rate that the heat obtained by the burning pyrite is sufficient to remove the sulphur, but not in larger quantities than to permit the cinders leaving the furnace, so cooled by the entering air that they do not show signs of glowing. The sulphur in pyrite which contain no other metals than iron, can be nearly completely burned off, only 1 per cent or less remaining. Any sulphur combined with copper or tin in the pyrite cannot be burned off.

Pure pyrite (FeS_2) contains about 53 per cent sulphur, but the commercial article only contains from 35 to 50 per cent.

In calculations on the use of pyrite, great care is necessary in order to avoid mistakes, because pyrite costs so much more than sulphur in handling, and the burner plant costs many times more than a sulphur burner plant. Some kinds of pyrite also contain elements like selenium, which cause serious trouble in the cooking, even when present in minute quantities.

If the pyrite can be delivered at the mill containing about 45 per cent of sulphur, or not less than 40 per cent of available sulphur, at a price per unit of sulphur in the pyrite amounting to about 60 per cent of the price of pure sulphur, it is generally good economy to use pyrite.

The washing and cooling of the gas is of particular importance when pyrite is used. The best arrangement is to conduct the gas through large vertical lead-lined pipes or towers which are provided with water sprinklers, which partly serve to remove the fine iron ore dust from the gas and also to keep the lead lining cool, as well as to some extent to cool the gas.

The wash water should be discharged at a temperature not less than 175°F. , because at lower tempera-

tures the water will retain SO_2 which will then be lost. It is best to arrange one washing system for each two Herreshoff burners. The gas is usually drawn through the burners and forced through washer and cooler into the acid making apparatus, by means of a fan. These fans are best made of phosphor bronze, and fitted with water-cooled bearings.

There are several types of gas coolers. Where a lead burner is employed, gas coolers can easily be made at the mill. The most suitable type of coolers are high, rectangular, horizontal lead pipes, stayed internally with lead pipes, and of such dimensions that the gas passes slowly through them. The stay pipes also serve the purpose of forcing the larger part of the gases to touch the sides of the water-cooled pipes, and are in themselves good coolers if not placed horizontally, as the cooling water passes through them quickly. The whole arrangement is placed in a tank supplied with cooling water, the flow of which is arranged on the countercurrent principle.

There are several types of coolers on the market which give very satisfactory results, but they are all very expensive.

The ordinary type of cooler, consisting of a great number of 8 or 10 in. lead pipes, arranged successively or in series in a water tank, is unsatisfactory, on account of the fact that the gas passes through too quickly, or in the case of a sectional arrangement of the pipes, it passes through only a part of the section, and thus the cooling surface is not properly utilized.

The coolers should be easily accessible for cleaning and repairs.

When pyrite is burned, the cooling surface should be about 15 square ft. per ton of daily production, and about this range of sulphur burners is used.

In summer time the gas should be cooled to nearly the same temperature as the cooling water before being admitted into the acid making apparatus. In winter time the cooling should be so adjusted that the temperature of the acid does not fall below 55°F. This is particularly important in connection with some of the limestone acid making systems, in order to keep the composition of the acid uniform all the year round.

The water obtained from these coolers, and the reclaiming coolers, can be used for diluting or washing the pulp as long as it is free from acid.

As already noted there are two distinct systems of acid making, the limestone system and the milk of lime system.

Of the first named there are four modifications employing high towers, low towers, tanks or chambers.

The milk of lime system consists of tank or low towers, but the chamber systems were, in early days, also used as a milk of lime system.

The merits of the different systems can only be judged in connection with each individual mill. As a rule the milk of lime systems are the most costly in running expense, on account of the cost of burning the

lime, but where the freight rates for lime and limestone are high, it must be considered whether the higher freight charges for the limestone, which is about 80 per cent heavier than the corresponding quantity of quicklime, would not pay for the burning of the lime at the quarry.

It was formerly thought that dolomite (MgCO_3) gave a better and whiter pulp than limestone (CaCO_3) whether burned or unburned, but this is not the case, so far as the limestone systems are concerned.

An equally strong and white pulp can be made by using limestone (CaCO_3) as by using milk of lime, but it is not possible to obtain a high quality of pulp with the milk of lime system, unless the lime contains about 33 per cent of magnesia (MgO).

Generally speaking it is of little importance for the composition of the acid, whether limestone or dolomite, a combination of (CaCO_3 and MgCO_3) is employed.

BLEACHING EXPERIMENTS WITH CHEMICAL PULP.*

In view of the publication in Nos. 95 and 96 of the *Papier-Zeitung* of a paper under the title of "Die Bleichende Wirkung von Chlorkalklösungen auf Zellstoff," by E. Sisonsen, the authors have been induced to publish the results of experiments carried out in 1906, on the same subject. The question was then studied more particularly from the industrial, or manufacturing point of view, rather than the chemical standpoint, and we have determined:

1. The rate of bleaching at constant temperature.
2. The rate of bleaching at varying temperatures.
3. The influence of residual bleach liquor on the economy of the process.
4. The influence of preliminary acid or alkaline treatment and the effect of adding the bleach in two portions.

The bleach was then added, and the observations taken as demanded by the nature of the trial.

This procedure was adopted in all cases, and was found to be all that was necessary when using an easy bleaching pulp. But in some later experiments, when using a strong non-bleaching sulphite, we found it impossible to obtain a uniform pulp in this manner. The half-stuff in such cases was obtained by breaking up the sheets in an experimental beater, making up to a known bulk and taking an aliquot portion.

5. The influence of the concentration of the pulp. The method adopted in carrying out the experiments to be described below was as follows:

Several sheets of the pulp chosen, which was a typical easy bleaching sulphate pulp, were allowed to become thoroughly air dry, representative samples

were taken for the moisture determination, and the remainder was cut up and carefully weighed out into 50 gm. lots. In conducting an experiment one of these lots was carefully torn up by hand into very small pieces, thrown into a known bulk of water, and the pulp obtained thoroughly churned with a strongly made egg beater fitted with teeth, until a finely divided and uniform pulp was obtained. This was filtered through a large porcelain funnel of about 8 in. diameter, the filtrate being poured through again until all the fine fibers were retained. The pulp was finally transferred to a 4-lb. stoppered bottle and sufficient water added to make it possible to mix effectively the contents by vigorous shaking after the addition of the bleach solution required by the condition of the experiment.

After bleaching, the pulp was filtered through filter paper by throwing on to the filter funnel, and the residual liquor exhausted by a water pump. The pulp was then washed with fresh water until the filtrate was free from chlorine by the starch iodide test. The first liquor and washings were made up to bulk, and the available chlorine estimated in an aliquot portion. The pulp left on the filter was washed with dilute acetic acid, and finally with water, until free from chlorine by the silver nitrate test, exhausted by the pump, air dried, and if the yield was required, finally oven-dried. In such cases a weighed filter paper was used above.

This method reduced the inevitable browning on drying to a minimum, and the pulp was available for making into sheets for reference.

In all our experiments tap water was used. It had a temporary hardness of 0 parts per 100,000.

The bleach is expressed in all cases as bleaching powder containing 35 per cent available chlorine.

Series I. Rate of bleaching at constant temperature.

Weight of pulp, 50 gms. air-dry; 46.03 oven-dry.

Concentration of pulp 1 in 16, when bleach is added.

TABLE I.—BLEACH TAKEN ON OVEN-DRY PULP, 18.15 PER CENT, TEMPERATURE 65° F.

Time Bleaching hours.	Bleaching on oven-dry pulp.	Color.
2	9.74	Poor
4	10.80	Not good
8	12.65	Good
12	14.31	Excellent
16	15.14	Excellent

The following curve plotted out with the time in hours as ordinates, and the percentage of bleach consumed on the oven-dry pulp as abscissa, illustrates in a more graphic manner the above results.

In this series of trials it will be noticed that a larger amount of bleach was added than necessary to bring the pulp to a good color, which would tend to exaggerate any action taking place and thus show what was going on more clearly. The bottles were placed in the dark during the period of bleaching.

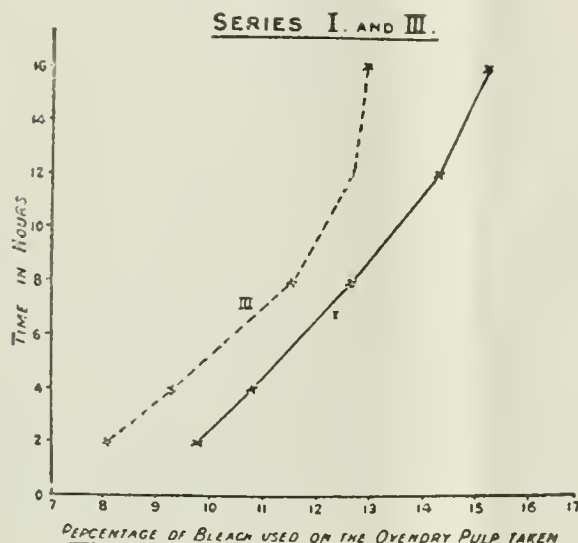
*From a paper presented before the London Section of the Society of Chemical Industry.

Series II. Rates of bleaching at variable temperatures.

TABLE II.—BLEACH TAKEN ON OVEN-DRY PULP, 18.15 PER CENT.

Temp. °F.	Per cent of bleach used on oven-dry pulp.	Time bleaching.	Color.
65	9.64	2 hrs.	Poor
100	15.05	2 hrs.	Excellent
120	17.45	2 hrs.	Excellent
140	18.15	80 mins.	Not good
160	18.15	50 mins.	Not good

The above series is strictly comparable with Series I. A curve plotted out below serves for comparison with that for Series I.



These figures show in a very clear manner how harmful is the action of high temperature upon the economy of the operation, and how deleterious with reference to the color of the bleached half-stuff. Yet one is sorry to say that in many mills this point seems to be entirely lost sight of.

We estimated the yield of bleached pulp in the foregoing series of experiments, and found the losses to be:

At 100° F. the loss was 1.684% on the oven-dry pulp taken.
At 120° F. the loss was 1.860% on the oven-dry pulp taken.
At 140° F. the loss was 2.191% on the oven-dry pulp taken.
At 160° F. the loss was 2.782% on the oven-dry pulp taken.

In Hofman's "Praktisches Handbuch der Papier-Fabrikation," second edition, there is mention on page 148 of some experiments conducted by Dr. Charles Cresson, who had repeatedly weighed pure wood cellulose before and after bleaching, and failed to find any discrepancy worth mentioning.

Our results on this head from Series II confirm what Cresson says, provided that the operation is carried out at a reasonable temperature.

On the large scale the loss between the half-stuff unbleached stage and the finished paper is anywhere about 3 to 5 per cent the bulk of which is due to loss of small fibers in handling.

On comparing the curve plotted out from the results obtained in Series No. I, with those published by Sindall and Heckford in the *World's Paper Trade Review* for December 2, 1904, on the rate of bleach consumption, we found that the rate of bleach consump-

tion in our trials was about 20 per cent higher than that obtained in their experiments. Thinking that possibly the large excess of bleach present in our case might have caused the rate to be accelerated in the earlier stages of the operation, we repeated the whole of that series, using an amount of bleach powder equal to the amount consumed during two hours at a temperature of 100° F. in Series No. II, viz., 15.05 per cent of bleach powder on the oven-dry pulp taken.

Series III. Rate of bleaching at constant temperature with less bleach present than in Series No. I.

TABLE III.—TEMPERATURE 65° F. BLEACH ADDED, 15.05 PER CENT.

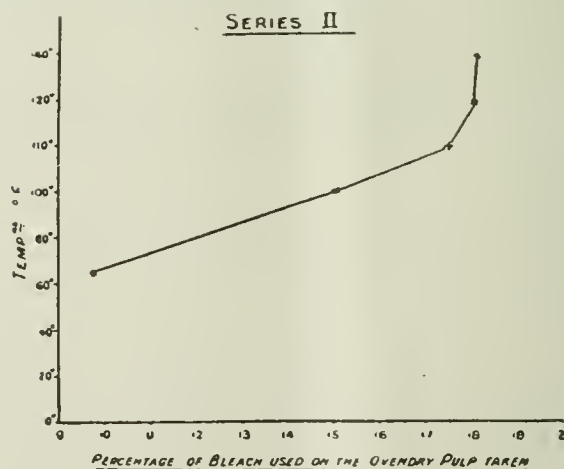
Time bleaching hours.	Bleach used on oven-dry pulp. Per cent	Color.
2	8.07	Very poor
4	9.33	Poor
8	11.56	Good
12	12.65	Excellent
16	12.82	Excellent

The results are plotted out below, against those obtained in Series I.

It will be observed that the curves are almost parallel until the later stages when the bleach consumption falls off slightly in Series No. III, showing that the relative rate of bleach consumption is the same until about twelve hours have elapsed.

The results seem to indicate that at this concentration of pulp there will always be about 10 to 20 per cent of the bleach added, left unconsumed in the residual liquors, if the bleaching is only carried on a reasonable length of time, i. e., not exceeding twelve hours at a temperature of 65° F., or for two hours at a temperature of 100° F.

Griffin and Little say in their book: "We have frequently tested the liquor in the chest, in order to determine the proportion of chlorine present after the



pulp had come to color, and have found in many cases it amounted to one-quarter or more of that originally introduced."

This is possibly quite common in many mills where it is the custom to use a fair excess of bleach to hasten the process.

We shall see later that the concentration of the pulp is a most important factor in hastening the time occupied for the bleaching operation, as well as reduc-

ing the waste of unconsumed bleach in the black liquor to a minimum.

On examining the colors of the bleached pulps obtained in Series I and II, we observed that the color of the pulp bleached for two hours at 100° F. and that of the pulp bleached for twelve hours at 65° F. were practically identical. Further, the amount of bleach consumed under the conditions of these two trials was approximately the same. We therefore decided that the other trials should be carried out at a temperature of 100° F. for a period of two hours, as this time and temperature were very convenient for conducting a number of experiments side by side.

It was explained above why an excess of bleach was taken in Series I and II. From the comparison of color and bleach consumption, it appeared that as far as economy went there was little to choose between bleaching for twelve hours at 65° F. or for two hours at 100° F., at any rate under the conditions of those experiments.

We therefore repeated the tests under the same respective conditions, but using the same amount of bleach as in Series III, viz., 15.05 per cent.

The results given below were confirmatory of the previous trials with a greater amount of bleach present. The slightly higher bleach consumption at 100° F. is probably explained by figures obtained in Series IV.

The conditions of the experiment were exactly the same as in Series III, the temperature and time varying.

TABLE III-A.—BLEACH ADDED 15.05 PER CENT.

Time bleaching.	Temp.	Per cent of bleach used on oven-dry pulp.	Color.
2 hrs.	100° F.	13.34	Excellent
12 hrs.	65° F.	12.65	Excellent

Series II'. The influence of residual liquors.

In this series the amount of bleach added was made up in one instance of part bleach contained in some back liquor obtained from a previous trial, and of part fresh bleach solution, the total amount being equal to 15.05 per cent on the pulp taken. The result of the test being compared with the standard obtained with the same amount of fresh bleach under the same conditions, i. e., two hours at 100° F.

TABLE IV.—BLEACH ADDED 15.05 PER CENT.

Per cent of bleach used on oven-dry pulp.	Color.
13.34	Excellent
14.47	Not so good

The bleach in the second experiment in Table IV was made by mixing 0.4519 gm. bleach in the back liquor with 6.4776 gm. in the fresh bleach solution.

From the foregoing results it is quite evident that some of the bleach in this experiment was used up by further action on the organic matter present in the back liquor, which action is no doubt accelerated by increased temperature.

Very possibly the slight increase of bleach consumption mentioned in Series III is accounted for on this ground, also taking into consideration the slight decomposition of the bleach itself which very likely takes place.

In order to further study the influence of back liquors, we made up solutions of fresh bleach, and a solution composed of part fresh bleach and part bleach contained in some mill back liquors.

The solutions were kept in the dark, contained in stoppered glass bottles, and tested periodically, with the following results:

TABLE V.

Time standing.	100 per cent fresh bleach. Loss per cent.	19 per cent bleach in the back liquor & 1 per cent fresh bleach. Loss per cent.
0 hours	—	—
48 hours	Nil	10.2
1 week	Nil	27.0
2 weeks	2.8	47.0

Fresh solutions made up on similar lines to the above were now tested for two hours at 100° F. and for two hours at 65° F. The available chlorine contents of the solutions used are given:

Solution 1 contained 0.7346 gm. of available chlorine from fresh bleach and 0.0098 gm. ditto from back liquor, made up to 300 cc.

Solution 2 contained 0.7346 gm. available chlorine from fresh bleach, made up to 300 cc.

TABLE VI.

Solution.	Time.	Temp.	Loss per cent.
1	2 hrs.	65° F.	11.80
2	2 hrs.	65° F.	Nil
1	2 hrs.	100° F.	23.13
2	2 hrs.	100° F.	0.47

These figures illustrate very clearly how uneconomical it is to use back liquors over again, and confirm some similar results published by Temperly (*Paper and Pulp*, January, 1901). Since no details are given of the strength of the solutions he employed, it is impossible to compare them in a satisfactory manner. Our results appear, however, to confirm his in a general way.

Series V'. The influence of preliminary alkaline and acid treatment, and of adding the bleach in two portions.

Seeing that we were dealing with the question from the standpoint of an easy bleaching pulp, we did not think it worth while trying the effect of a preliminary washing with water, as a pulp requiring such treatment on the large scale could not be classified as an easy bleaching one.

Afterwards, however, we examined the water extract from the unbleached pulp on which the trials had been made with reference to the amount of bleach which the faintly colored water extract would account for.

Fifty grams of the air-dry pulp were extracted with 1½ liters of cold water. Two separate 500 cc. were taken to which was added 50 cc. of bleach solution of a known strength. During the time the solutions were under observation, one was kept at 100° F. and the other at 65° F.; 50 cc. of bleach solution contained 2.3399 gm. 35 per cent bleaching powder.

TABLE VII.—LOSS PER CENT ON THE BLEACH ADDED.

Solution.	Temp.	2 hrs.	4 hrs.	5 hrs.
1	100° F.	5.58	5.58	5.58
2	65° F.	4.29	4.29	4.29

These are the losses caused by the extract contained in 500 cc., therefore, if the whole extract had been taken the losses would have been trebled.

The figures show that a certain amount of bleach is consumed in oxidizing organic matters which could be extracted by washing with water, but as the economy thus effected would, in the case of a pulp requiring say 12 per cent bleach, only amount to 15 per cent of 12 per cent, *i. e.*, 1.8 per cent bleach on the pulp taken, it is hardly worth the time and trouble that would have to be spent on it during the washing process.

The amount of bleach consumed by the wash waters of the pulp we had under consideration are very closely in agreement with the 1.5 per cent obtained by Sindall and Heckford in experiments conducted on somewhat similar lines (see *Paper Trade Review*, October 7, 1904).

Our results show that the extract is rapidly oxidized, after which little action goes on in the way of decomposing the remaining bleach.

We thought, however, that it might be worth while trying if any economy could be effected by a preliminary acid or alkaline treatment. With an easy bleaching pulp like the one under consideration the results were disappointing, for although the color was much improved by the acid treatment in the case of soda pulp and by alkali treatment in the case of sulphite pulps, the economy effected in the bleaching consumption was insignificant. The acid treatment consisted in saturating the pulp with a solution of hydrochloric acid in amount equal to 1 per cent on the weight of air-dry pulp, which was allowed to stand two hours. The pulp was then washed on the filter until the filtrate was free from chlorides when the pulp was ready for bleaching in the usual way. The alkali treatment was effected in exactly the same manner, 1 per cent caustic soda being used on the air-dry pulp taken.

In the trial where the bleach was added in two portions, the second lot of bleach was added immediately after the first was consumed. This latter trial was undertaken because it is still the practice in some mills to add the bleach in this manner, without first washing out the products extracted by the first lot of bleach. The results are instructive, and only what one would expect from a consideration of the earlier trials with back liquor.

TABLE VIII.—ALKALI AND ACID TREATMENT. BLEACH ADDED, 15.05 PER CENT.

Per cent of bleach used on oven-dry pulp.	Color.	Treatment.
13.34	Excellent	None
12.80	Excellent	Alkaline
12.80	Brilliant	Acid
12.80	Not so good	Bleached in two portions

The color of the bleached pulp that had had a previous acid treatment was brilliant in comparison with the others, the pulp having had a previous alkaline treatment being a good second. In the trial in which

the bleach was added in two portions the color was poor. In the latter case the bleach was added in two equal portions, the first lot being exhausted in 40 minutes.

Series VII. The influence of the concentration of the pulp.

We were well aware from numerous experiments that this factor is perhaps the most important one in the bleaching of material in the pulp state. Indeed, one might say that it is impossible to obtain the highest economy without careful attention to this most vital point.

Sindall and Heckford emphasize this in their remarks on the subject, as also do Cross and Bevan in their textbook on papermaking, but do not give any data bearing on the question.

The former investigators say in an article published in the *Paper Trade Review*, September 16, 1904:

"This question of the proportion of water in relation to the bleach consumption is really an important one. The influence of the quantity of water used per cwt. pulp in the beater is not so fully appreciated by paper makers as it should be, and a few definite trials under carefully regulated conditions would soon convince them that the operation of bleaching wood pulp is not such a simple matter of routine after all. 'More water more bleach' is a common expression, and a common experience, but it is a fact that has not been properly studied. We are ready to accept the idea that the extra bleach is simply consumed by the extra water itself. But the amount used is always considerably in excess of that actually required to neutralize the water, and we are forced to seek some better explanation. Probably the active bleach in solution attacks the chlorinated organic compounds formed during the process, and the actual bleaching of the pulp is retarded, so that not only

TABLE IX.—TEMPERATURE, 100° F. TIME, 2 HOURS. BLEACH ADDED, 15.05 PER CENT.

Per cent of bleach used on oven-dry pulp.	Concentration.	Color
11.86	1.24	Very poor
13.34	1.16	Excellent
14.04	1.12	Brilliant

is the consumption of bleach greater, but the period occupied is longer."

We conducted three trials at different concentrations of the pulp, the intermediate one being the same concentration used throughout all the experiments detailed above.

The results are not only of interest, but we think of value, showing that the idea that the bleach is consumed by the water, or that it is used up in attacking chlorinated organic compounds, is erroneous, as the foregoing trials show conclusively that the bulk of the bleach is simply left unchanged in the back liquor.

The old mill maxim "more water more bleach" is thus founded on fact. The explanation appears to be, that in weak solution the action is not sufficiently energetic to cause a reasonable exhaustion of the avail-

able chlorine. In other words, it is a case of mass action.

All the experiments described were conducted on an easy bleaching so called soda pulp, which was really a sulphate pulp. We found, however, that the results obtained applied equally well with reference to easy bleaching sulphite pulps, with the exception already mentioned that with a preliminary alkaline treatment the color obtained after bleaching was much better than that given by a preliminary acid treatment.

The net result of the work we have carried out is as follows:

1. That the use of back liquors is attended with an increase in the bleach consumption, and accompanied by a lowering of the color of the resultant bleached pulp.

Its only legitimate use is in the early washing of boiled rags, or similar operations, prior to bleaching, when it can be thoroughly removed before the bleach is added to the clean half-stuff.

2. That preliminary washing either by water, dilute acid, or dilute alkali, is not worth while in the case of easy bleaching pulps.

3. That the concentration of the pulp is the most important factor to be taken into consideration, and due regard to this point is absolutely essential in order to obtain the highest economy in the bleaching process as carried out in the paper mill.

4. That when bleaching with the aid of heat, a temperature of 120° F. should not be exceeded, our results tending to show that temperature of 100° F. is all that is necessary. Wherever possible the pulp should be heated before the bleach is added, as, if heated when the bleaching is going on, there must always be excessive local heating of the pulp, even if a fairly rapid circulation of the stuff is maintained, of course detracting from the economy of the operation.

Due regard having been paid to the above points, it is a matter for consideration whether the operation is best carried out at 100° F., or at say the temperature of the atmosphere. It is simply a question of cost of equipment.

In bleaching at 100° F. it is tolerably certain that it will be necessary to circulate the pulp during the greater part of the time it is bleaching, whilst practice has shown that when bleaching for a considerable length of time in the cold, occasional agitation is all that is necessary, in spite of teaching to the contrary. Some manufacturers have realized this, and it is modern practice to fit bleaching pots with fast and loose pulleys in order to economize power.

All work upon the subject of bleaching pulps leads one to the point: Why is there not a standard method of bleaching pulp, and standards of color for reference in cases of dispute? There can be no question that a standard method would meet with general approval. Various investigators have raised the question, and it has even been discussed by the Wood Pulp Association. As Sindall and Bacon point out in

their work, "The Testing of Wood Pulp," the real difficulty is not the method of performing the operation, but rather the difficulty of fixing suitable standards of reference. They put forward in a tentative sort of way the suggestion that the use of Lovibond's Tintometer might meet the case, but it has apparently found little support. Whilst the tintometer is a useful instrument in the hands of a skilled operator for certain purposes in other industries, it is our opinion that such a method for measuring the color of bleached wood pulp is extremely unlikely to find favor in the pulp and paper industries, not because of any inherent defects in the proposed method of judging color value, but simply because the type of man who usually sells and buys pulp would be the last person to pay any attention to such a highly technical method of stating color value.

Looking at the subject from a practical point of view, one must arrive at the conclusion that any standard test which will find general acceptance must be simple and easily understood by the commercial man, on the point of reference to color value. Settle this point, and a standard method of procedure in the actual bleaching test itself will soon be agreed upon by all interested.

We therefore suggest that four standards of color should be fixed by suitable representatives of pulp and paper manufacturers. These standards to be matched in dull porcelain as follows:

- A. Color obtained by first quality easy bleaching sulphite.

- B. Color obtained by second quality easy bleaching sulphite.

- C. Color obtained by first quality easy bleaching sulphate.

- D. Color obtained by second quality easy bleaching sulphate.

Under the conditions of the standard test given below. Standards to be kept by the Paper Makers' Association and the Wood Pulp Associations of the various countries as official standards. The buyer would then be enabled to contract for a bleaching pulp with a specific clause in his contract to the effect that the pulp mentioned would give under the conditions of the standard test a color of A, B, C or D, with a stated percentage consumption of bleaching powder. In a case of dispute, the arbitrators would then have available a recognized standard of bleaching quality, and would not be compelled to fall back upon what is commercially known as the "brand," whatever that may happen to mean in any particular case.

Each paper maker and pulp seller would be able to provide himself with similar standards to the official ones, and once knowing the percentage of bleach powder required to produce a color represented by any one of the four standards could, by a glance at his color standards, readily form an estimate of the value of any pulp so far as its bleaching qualities were concerned.

THE DISTRIBUTION OF HEAT IN THE OPERATION OF STEAM BOILERS.*

By PERRY BARKER.

In combustion of coal in boiler furnaces a comparatively large percentage of the heat in the fuel is not usefully employed. The extent of the losses which affect the boiler efficiency is governed by (a) the design and physical condition of the plant, (b) the personal element in the operation of the boilers, (c) the character and adaptability of the fuel for the plant in question, and (d) the rate of steam generation or capacity at which the boiler is operated. The efficiency with which fuel is burned is controlled by these factors, and excessive losses may be due to one or a combination of them.

The Power Tests Committee of the American Society of Mechanical Engineers, recommended that a balance accounting for the distribution of heat in a pound of dry coal fired consist of the following items:

1. Heat absorbed by the boiler.
2. Loss due to evaporating and superheating moisture in coal.
3. Loss due to evaporating and superheating moisture formed by the combustion of hydrogen and distillation of oxygen-hydrogen compounds in the coal.
4. Loss due to heat carried away by dry flue gases leaving the boiler.
5. Loss due to heat escaping through the formation of carbon monoxide (CO).
6. Loss due to combustible removed from ash pits and from grates during cleaning.
7. Loss due to superheating moisture in the air used for combustion.
8. Loss due to unconsumed hydrogen and hydrocarbon, to radiation, and unaccounted for.

Items 4, 5 and 6 generally cover about 75 per cent of the total heat lost, and are the variable factors which have a direct effect on the percentage of heat imparted to the water in the generation of steam. In presenting certain data on these losses, illustrations of the origin, extent and methods which have been employed for their reduction, are submitted.

The loss generally largest and in most cases easily reduced, is the heat carried away by the dry flue gases. Under this heading are included the sensible heat in the carbon dioxide and carbon monoxide formed by the combustion of the carbon in the fuel, and the heat in the air in excess of that theoretically required, leaving the boiler at the temperature of the escaping gases.

The principal causes of this loss are as follows:

- (a) Improper methods of firing, allowing large quantities of air to enter the furnace either through the grates or fire doors.
- (b) Condition of boiler settings. If the settings are cracked and the iron work warped, the air drawn

through these openings, reduces the draft at the grate, and dilute and cool the gases as they pass over the heating surface.

(c) Poor quality coal. Coals containing high percentage of ash or having a tendency to clinker cause an uneven distribution of the air through the fuel bed. When such a condition exists, excess air enters the furnace and carried away heat in the flue gases. If the fuel is too fine, it will pack on the grate and produce a similar effect.

This loss depends upon the weight of gases per pound of carbon burned and the temperature at which these gases leave the boiler. The data required for this computation are the temperature of the flue gases, temperature of the boiler room, composition of the flue gases, heating value of the coal, and the carbon content of the fuel and ash pit refuse.

Some tests in a plant where loss of heat in the flue gases was originally high are shown in Table I. They were hand-fired horizontal return tubular boilers equipped with plain grates, burning Pennsylvania semi-bituminous coal containing about 9.00 per cent of ash and 22.00 per cent of volatile. The fires were carried at a thickness not exceeding 7 inches and were uneven, thereby permitting large air excess. The thickness of the fire was then increased and the method of firing altered resulting in a reduction of the loss due to excess air from 36 to 12 per cent, with an increase of 20 per cent in boiler efficiency. The tests showed that the air excess in the latter tests was lower than could be recommended for regular operation, as considerable carbon monoxide was formed.

TABLE I.—LOSS DUE TO HEAT CARRIED AWAY BY DRY FLUE GASES LEAVING THE BOILER.

	Original conditions. Per cent.	Tests to improve efficiency. Per cent.	
		10.0	12.4
1. Heat carried away by dry flue gases...	35.9		
2. Evaporating and superheating moisture in coal, and moisture formation of carbon monoxide	0.0	0.4	1.6
3. Evaporating and superheating moisture formed by combustion of hydrogen and distillation of oxyhydrogen compounds	2.7	2.7	2.8
4. Loss in combustible removed from the ash pits and from grate during cleaning	3.2	7.6	4.5
Total determined loss	41.8	20.7	21.3
5. Other losses (assumed constant for all tests)	8.9	8.9	8.9
6. Approximate percentage of heat absorbed by the boiler or boiler efficiency (by difference)	49.3	70.4	69.8
Total	100.0	100.0	100.0

The loss of heat due to the incomplete combustion of carbon to carbon monoxide, is usually important. Carbon monoxide in flue gases is generally accompanied by tar vapors or particles of solid carbon (smoke), together with small percentages of unburned hydrogen and hydrocarbon gases. Its formation is due to the following causes:

- (a) Furnaces of poor design.

*Paper presented at the Boston meeting of the American Institute of Chemical Engineers.

(b) Improper firing.

(c) The character of the fuel, particularly with reference to the equipment in which it is burned.

While the presence of CO shows that some heat is being lost by incomplete combustion, a small percentage of this constituent generally indicates that the air excess is reduced as low as practicable. A small amount of smoke, as evidence of presence of carbon monoxide, is a better indication of economical furnace operation than a smokeless stack, which may be emitting several hundred per cent of excess air.

The extent of this loss is dependent upon the percentage of carbon monoxide (CO) and carbon dioxide (CO₂), as determined by the flue gas analysis, the heating value of the coal, and the percentage of carbon in the coal fired and in the ash pit.

Tests in a plant where loss due to unburned gases (indicated by the CO) was particularly high, are shown in Table II. These were hand-fired vertical tubular boilers, with shaking grates, burning Georges Creek coal, containing 18.00 per cent of volatile. The incomplete combustion was not attributed to the coal, although the furnace space was not sufficient to burn coals containing high percentages of volatile matter without an excessive amount of smoke. Aside from furnace design, the primary cause of high CO was the thickness of the fires. By reducing the thickness from 30 inches to 12 inches, and changing the way of firing, this loss was reduced from 14 to 1 per cent, with a corresponding increase in boiler efficiency.

In firing a boiler a certain percentage of the fuel fed drops through the grate and is removed with the ashes, and additional unburned coal is drawn from the grates in hand-firing, when the fires are cleaned. The amount of fuel thus lost depends on: (a) The character of the coal; (b) the condition of the equipment; (c) the method of handling the fires.

If the coal is fine or non-caking and the grates contain large air spaces, excessive amounts of fuel drops through. Some coals clinker badly, and during

the removal of this clinker quantities of unburned coal are drawn from the fires. The frequent barring or raking of fires when using fine or non-caking coal, is another cause of loss.

For computing ash pit loss, which includes the combustible removed during cleaning, the heating value of the combustible is taken as 14,600 B. T. U. per pound. In cases where complete boiler tests are not made, and the weights of coal and ash pit refuse are not taken, the fuel removed with the ashes and cleanings can be computed from an analysis of this material and the percentage of ash in the coal fired. In calculating this by the latter method, the assumption must be that the percentage of ash obtained by the proximate analysis of the fuel represents the inert matter in the refuse from the ash pits and the furnace; that is, no account is taken of the ash carried off the grates and deposited in the combustion chamber, upon the water heating surface or carried up the stack. A series of tests, indicating how much this loss can be reduced are submitted in Table III. This plant had inclined grate stokers, burning Pittsburgh slack coal. The excessive rate at which the fuel was burned, in order to maintain the required capacity, caused deterioration of the grates, allowing large quantities of unburned coal to fall into the ash pits. By careful attention to grate repairs and methods of operating the stokers, the boiler efficiency was increased 10 per cent.

TABLE III.—LOSS DUE TO COMBUSTIBLE REMOVED FROM ASH PITS AND FROM GRATES DURING CLEANING.

	Original conditions. Per cent.	Tests to improve efficiency. Per cent.	
1. Loss in combustible removed from the ash pits and from grate during cleaning	13.1	9.1	7.9
2. Loss due to evaporating and superheating moisture in coal and moisture formed by the combustion of hydrogen and distillation of oxyhydrogen compounds	3.2	3.3	3.1
3. Heat carried away by dry flue gases, ...	22.8	19.1	18.2
4. Heat escaping through the formation of carbon monoxide	0.0	0.0	0.0
Total determined losses	39.1	31.5	29.5
5. Other losses (assumed constant for all tests)	7.5	7.5	7.5
6. Approximate percentage of heat absorbed by the boiler or boiler efficiency (by difference)	53.4	61.0	63.0
Total	100.0	100.0	100.0

The percentage of hydrogen in coals is not an indication of their relative value when burned for the generation of steam. The essential feature in determining the effect of this constituent in the process of combustion, is the form in which it is available. Hydrogen, driven off in the uncombined state and burned by mixing with the oxygen from the air supply, is a valuable factor in combustion, as it develops about four times the heat generated by an equal percentage

TABLE II.—LOSS DUE TO HEAT ESCAPING THROUGH FORMATION OF CO.

	Original conditions. Per cent.	Tests to improve efficiency. Per cent.	
1. Loss due to heat escaping through the formation of carbon monoxide (CO.)	15.3	1.1	2.1
2. Loss due to evaporating and superheating moisture in coal and moisture formed by the combustion of hydrogen and distillation of oxyhydrogen compounds	4.1	3.8	4.2
3. Loss due to heat carried away by the dry flue gases	9.7	15.1	10.7
4. Loss in combustible removed from the ash pits and from grate during cleaning	3.2	3.5	3.3
Total determined loss	32.3	23.5	20.3
5. Other losses (assumed constant for all tests)	11.2	11.2	11.2
6. Approximate percentage of heat absorbed by the boiler or boiler efficiency (by difference)	56.5	65.3	68.5
Total	100.0	100.0	100.0

of carbon. However, a certain percentage of the hydrogen is distilled from the bituminous matter in the form of tar vapor and water. The nature of these compounds has been ascertained when coal is subjected to destructive distillation, as in the manufacture of illuminating gas, but the transformation through which this portion of the hydrogen passes in the boiler furnace, is as yet undetermined. For the purpose of this discussion the theory of the code of the American Society of Mechanical Engineers, for conducting steam boiler trials, for the loss due to hydrogen, is accepted. This theory assumes that all hydrogen contained in the fuel, together with an equivalent amount of oxygen in the form of water, is raised from boiler room temperature, evaporated in the furnace, and superheated to the temperature of the escaping gases. The amount of heat thus lost depends upon the composition of the fuel, the temperature of the boiler room and the temperature of the escaping gases. In addition to the loss due to evaporating and superheating the moisture formed by the combustion of hydrogen and by the distillation of oxyhydrogen compounds, a small loss is incurred by heating the moisture in the fuel and in the air used for combustion.

Increasing interest in the economical operation of boiler plants has resulted in marked improvement. The distribution of heat in a plant operated with high efficiency before tests were made for contemplated improvement is shown in Table IV.

TABLE IV.—PLANT OPERATED WITH HIGH EFFICIENCY.

	Original conditions. Per cent.	Tests to improve efficiency. Per cent.	
		Original conditions. Per cent.	Tests to improve efficiency. Per cent.
1. Evaporating and superheating moisture in coal and moisture formed by the combustion of hydrogen and distillation of oxyhydrogen compounds....	4.0	3.8	3.8
2. Heat carried away by the dry flue gases	14.4	10.1	11.8
3. Heat escaping through the formation of carbon monoxide	0.9	1.3	0.4
4. Loss in combustible removed from ash pits and from grate during cleaning.	0.6	0.8	0.9
Total determined losses	19.9	16.0	16.9
5. Other losses (assumed constant for all tests)	8.0	8.0	8.0
6. Approximate percentage of heat absorbed by the boiler or boiler efficiency (by difference)	72.1	76.0	75.1
Total	100.0	100.0	100.0

It had large units of Climax water tube boilers with circular grates fired through a number of doors. Considerable loss due to the formation of CO is shown, but this is more than balanced by the particularly small percentage of combustible removed from the ash pits and furnaces. The amount of combustible in this material averaged 12 to 15 per cent, representing a fuel loss of from 0.5 to 1 per cent. Although the operating conditions in this plant were excellent, greater care in firing effected an increase in boiler efficiency.

THERMIT WELDING: DEVELOPMENT AND APPLICATION IN RAILWAY SHOP PRACTICE.*

The fact that aluminum is hard to separate from oxygen is taken advantage of in the Thermit reaction as the high affinity of aluminum for oxygen permits of a chemical reaction between the two when they are heated hot enough. Chemists for many years since aluminum was discovered have known of this reaction and experimented with it in the reduction of different oxides, mixing finely divided aluminum with a metallic oxide, placing the mass in a crucible and then heating it until the reaction took place. It was found that this resulted in a very violent reaction, practically an explosion, so that the reaction was of no commercial value. Dr. Hans Goldschmidt, a German chemist, and metallurgist, discovered that this reaction could be controlled if instead of heating the entire mass he simply heated the mass in the crucible at one spot. The reaction would then spread through the rest of the mixture and at the end of the reaction he would have aluminum oxide or slag floating on top in a molten state and the reduced metal at the bottom of the containing vessel. This discovery was the result of experiments by Dr. Goldschmidt who was attempting to produce for the famous firm of Krupps, the steel makers in Germany, pure metals to use as alloys with steel, and the first experiments were made with chromium oxide and finely divided aluminum. This reaction was entirely successful, as aluminum combined with the oxygen in the chromium oxide and pure chromium metal was reduced. He later experimented with other oxides, sulphides and chlorides and succeeded in producing pure manganese, ferro-chromium, molybdenum, ferro-titanium and many other metals and alloys.

Among other oxides experimented with was iron oxide, but he found that this reaction not only produced a very pure, low carbon steel, but that the heat of this reaction was extremely high. No pyrometer will measure this temperature, but it has been worked out theoretically by Professor Richards of Lehigh University as approximately 4,881 degrees Fahrenheit. Dr. Goldschmidt decided that this intense heat, produced so quickly and easily, could be used in many ways for welding purposes, and the Thermit welding process which is now so widely known throughout the world is the result.

In making a Thermit weld the parts to be united are first arranged with a space between them varying from one-half inch to two or three inches, depending upon the size of the sections. Where the pieces to be welded are in two parts it is a simple matter of course, to provide the space but in the case of a fracture it is often necessary to cut out the metal in order to provide the space needed, and this is done by drilling a line of holes along the fracture and then

*From a paper by W. R. Hulbert and H. D. Kelley, presented before the Railway Club of Pittsburgh.

cutting out the metal between the holes or else the space is cut out by means of the oxyacetylene cutting flame.

In the case of welding locomotive frames it is almost always necessary to cut out the fracture. The acetylene cutting flame is the most efficient and generally used medium.

After the sections have been cut out a wax pattern is formed around them of the exact shape of the reinforcement of Thermit steel which is to be cast around them to make the weld. Thermit, as already explained, is a mixture of aluminum and iron oxide which, when ignited, reacts. The aluminum combines with the oxygen of the iron oxide while the iron is set free and comes down as a highly superheated liquid steel at a temperature of nearly 5,000 degrees Fahrenheit, or about twice the temperature of ordinary molten steel. It will readily be seen that if we pour this steel around the sections to be united, it will melt those sections and amalgamate with them so that the whole will cool down to form a single homogeneous mass.

The wax pattern mentioned above is enclosed in a sand mold, wooden patterns being used for a pouring gate, a small preheating opening at the bottom and a large riser directly over the top of the weld. These wax patterns offer many advantages over wooden patterns which are sometimes used, as they do away with the necessity of making the mold in two parts. In order to remove the pattern it is only necessary to apply the flame of a compressed air gasoline preheater to the preheating opening and the wax is melted out, leaving the mold ready for pouring. For that part of the mold which comes in contact with the Thermit steel we use a mixture of one-third fire clay, one-third ground fire brick and one-third good sharp silica sand. This is mixed dry and then moistened just enough to tamp well. This is only used for the facing material and is backed up with a mixture of one-third fire clay and two-thirds sand. After the wax is melted out by the preheater the heating is continued until the parts to be welded have been brought to a good red workable heat. In the meantime the charge of Thermit is placed in a conical shaped crucible suspended over the pouring gate of the mold and when the sections are red hot the preheater is withdrawn, the opening plugged up and the Thermit charge in the crucible ignited. In from 40 to 50 seconds the Thermit reaction is completed and the Thermit steel tapped from the bottom of the crucible into the mold where it flows around and between the sections to be welded together, uniting them into one solid mass. The slag (aluminum oxide) does not enter the mold but overflows it so that it does not interfere with the welding operation.

It will be seen that the process is a simple one and that the only outside power required to weld sections of any size is a small supply of compressed air for

the operation of the preheater. The outfit is entirely portable and in many cases sections of very large size are welded without removal from their position, and therefore at a great saving in time and expense over obtaining new parts or repairing by other means. This is particularly advantageous in the case of broken locomotive frames. It saves taking the frame out of the engine, welding it in a forge and replacing it. Furthermore the process permits of fusing a collar or reinforcement of steel all around the welded part, thus increasing the cross-section at that point and making it stronger than it was originally.

In welding a locomotive frame it is necessary to jack the frame apart about one-eighth to three-sixteenths of an inch before putting on the mold in order to allow for the contraction of the Thermit steel when the metal in the weld cools. Where one part of a double barred frame is being welded this contraction is allowed for by heating up the other section so as to expand it the required amount and holding that heat until the metal in the weld has solidified, after which the heat can be taken off and both sections will cool down and contract together. In the case of locomotive frames broken in splices, it is usually found that the break is through a bolt hole, that being a weak point in the splice.

The great economy of the process in locomotive repair work has led to its adoption by practically all the railroads of consequence in the United States, Canada and Mexico and the process is now used in 421 different railroad shops in North America.

Very little stripping of the engine is required for a Thermit weld, as it is only necessary to provide a clearance of about one foot all around the broken section. In fact it is usually only necessary to drop the driving wheels in order to effect a repair on a broken frame. Often the engine comes into the shop in the morning and twelve hours later the frame will be welded and the locomotive ready for service.

It is not only on locomotive frames that Thermit finds extensive use in railroad shops, as it can be applied to equal advantage in the welding of broken driving wheel spokes, side rods, connecting rods, rocker shafts, cross head guides, cylinder saddles, mud rings and other broken sections too numerous to mention.

It is in rail welding that the Thermit Process offers its greatest field of usefulness to street railway companies, as the apparatus is simple in the extreme and enables a few joints to be welded almost as cheaply as a large number.

Street railway companies are realizing more and more the importance of installing permanent joints in place of mechanical joints and welding is the only means to attain that end. The life of the rail depends very greatly on the efficiency of the joint as the rails always wear out and batter where the joints occur.

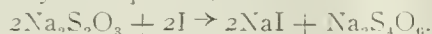


METHODS OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR INSTITUTE OF TECHNOLOGY.

Laboratory Standard Solutions (Continued).

IODIMETRIC SOLUTIONS.

The fundamental reaction of iodimetry may be expressed by the equation,



From this, one molecule of sodium thiosulphate is equivalent to one atom of iodine, and since one iodine is equivalent to one hydrogen,

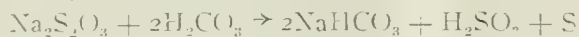


Normal solutions of iodine and sodium thiosulphate, therefore, contain, per liter of solutions, one gram atom of the former and one gram molecule of the latter. Since tenth normal solutions are ordinarily used,

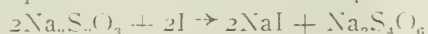
$$\text{N}/10 \text{ I} \equiv 12.69 \text{ gms. per liter}$$

$$\text{and } \text{N}/10 \text{ Na}_2\text{S}_2\text{O}_3 = 15.82 \text{ gms. per liter.}$$

Since sodium thiosulphate carries $5\text{H}_2\text{O}$ per molecule, 15.82 gms. $\text{Na}_2\text{S}_2\text{O}_3$ is equivalent to 24.82 gms. of the crystalline salt. For the tenth normal solutions, therefore, 12.8 gms. of pure iodine are weighed out for each liter of solution, and 24.9 gms. of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. The thiosulphate crystals are dissolved, and the solution made up to the required volume with distilled water. This solution should be kept for from ten days to two weeks before standardization, because the dissolved carbon dioxide invariably present in the water reacts with some of the thiosulphate according to



and the sulphurous acid formed reacts with iodine in the subsequent titration, using more of the latter than the equivalent amount of thiosulphate, because



whereas $1\text{H}_2\text{SO}_3 + 2\text{I} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + 2\text{HI}$.

When the carbon dioxide in the water is completely used up in the above reaction, the resulting solution should be permanent for almost a year, though it is well to check the standard occasionally. The small precipitate of sulphur should be disregarded, as it does no harm.

The iodine solution is made up as follows: The proper weight of pure crystals is weighed out and triturated with water in a mortar, together with about twice its weight of pure potassium iodide, the solution being poured off and more water added until the iodine is completely dissolved. The KI should be

added a little at the time. The solution is then made up to volume and thoroughly mixed. Iodine solution is not nearly so permanent as thiosulphate solution. One may always observe iodine vapor over the solution in the bottle, which shows that there is a constant escape of iodine with corresponding weakening of the solution. (The fiftieth or hundredth normal solution frequently employed in the determination of sulphur in iron and steel is much more stable than the usual decinormal). It is necessary, therefore, to check the standard of the iodine frequently against the permanent thiosulphate solution.

The indicator used in the processes of iodimetry is starch, which unites with a minute amount of iodine forming the fine, blue "iodide of starch." The amount of iodine necessary to give this blue color, even in very dilute solution, and the corresponding amount of thiosulphate required to decolorize the solution, is so minute, that this reagent furnishes one of the most delicate end reactions known.

For the indicator, 0.5 gm. of starch is mixed with a few cc. of cold water and the mixture poured into 100 cc. of boiling water and the whole boiled for a few minutes, until the solution is practically clear. This solution should not be kept more than three or four days, for it moulds readily, and loses its delicacy as indicator. Where a great deal of it is to be used, it may be worth while to prepare a liter of starch solution and bottle it in small bottles, which are stoppered and sterilized by long heating in the waterbath. The so-called "soluble starch" which may now be obtained is convenient, for it needs only to be dissolved in cold water. Three (3) cc. of indicator should be used for all titrations.

Either the iodine solution or the thiosulphate may be directly standardized. It is much better however to standardize the thiosulphate, and calculate the standard of the iodine from its relationship to the thiosulphate, because the methods are more accurate and also more convenient.

In general, iodine solution is used as an oxidizing agent to titrate reducing agents. Thus, it may be employed in the determination of arsenic and antimony, for in alkaline solution, it oxidizes the trioxides to the pentavalent condition.

Thiosulphate solutions are used in general for the determination of those substances which liberate iodine directly or indirectly according to a definite reaction, from potassium iodide. These substances are for the most part oxidizing agents.

Standardization.—The relationship of the thiosulphate and iodine solutions is first determined by titrating the one with the other to constant result. After this, the thiosulphate may be standardized by a variety of methods. Of these, the permanganate, the dichromate, and the copper methods are recommended. The direct standardization of the iodine by means of arsenic trioxide is not recommended.

Standardization Against Standard Permanganate Solution.—Potassium permanganate reacts with potassium iodide in the presence of hydrochloric acid in the cold, rapidly and completely, with the liberation of iodine according to the equation

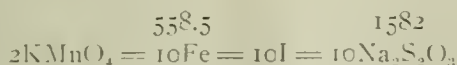


From this, and since 2KMnO_4 is equivalent to 10Fe in acid solution,



The procedure: 2 gms. of potassium iodide crystals is placed in a 400 cc. beaker and dissolved in a little water. To this is added 10 cc. of 1:5 hydrochloric acid, and then 40 cc. of the standard permanganate solution (about tenth normal) run in from the burette. Finally the whole is diluted to about 200 cc. and titrated to a light yellow color with the thiosulphate solution, starch (3 cc. of solution) added, and the titration finished. The end point may be taken either as the decolorization of the blue iodide of starch, or the first blue color upon the back titration of a small excess of the thiosulphate. The latter is recommended.

The calculation: Since



and the weight of iron represented by the permanganate is 40x, the iron standard, then

$$558.5 : 1582 :: \text{wt. of Fe} : x$$

$$1282 \times \text{wt. of Fe}$$

$$x = \frac{1282 \times \text{wt. of Fe}}{558.5} = \text{wt. Na}_2\text{S}_2\text{O}_3 \text{ equivalent to}$$

$$559$$

the permanganate used, and this weight divided by the net volume of thiosulphate solution gives the

$$\text{Wt. per cc.}$$

$$\text{weight of Na}_2\text{S}_2\text{O}_3 \text{ per cc.} = \frac{\text{Wt. per cc.}}{0.01582} = \text{factor of}$$

N/10 of the solution. From this data and from the ratio of the thiosulphate solution to the iodine solution, the standard and the normality of the iodine solution is calculated.

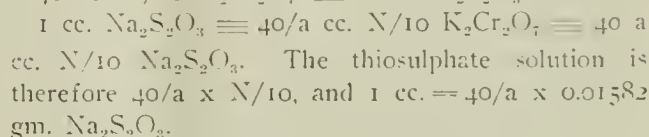
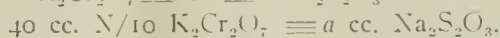
Standardization by Means of Potassium Dichromate.—Potassium dichromate oxidizes potassium iodide in the presence of hydrochloric acid instantly and completely with the liberation of iodine according to the following equation: $\text{K}_2\text{Cr}_2\text{O}_7 + 6\text{KI} + 14\text{HCl} \rightarrow 8\text{KCl} + 2\text{CrCl}_3 + 7\text{H}_2\text{O} + 6\text{I}_2$. The liberated iodine is titrated with sodium thiosulphate.

The following conditions give excellent results:

A tenth normal solution of potassium dichromate is

prepared by weighing exactly 4.903 gms. of the pure salt and making it up to exactly one liter at the correct temperature. 3 gm. of potassium iodide is dissolved in water in a large beaker, 20 cc. of 1:1 hydrochloric acid is added, and 40 cc. of the dichromate solution run in from the burette. The whole is then diluted to a bulk of not less than 400 cc. and the liberated iodine titrated. The chromic chloride formed as a product of the reaction has a clear bluish green color, and would seem to interfere with the blue iodo-starch reaction. One needs to make the titration but once to realize that the end-point is as well defined in the presence of this color as in a colorless solution. The large bulk of solution is used to make the color as light as possible. This method is particularly recommended. The dichromate solution is permanent, and may be prepared by direct weight with great accuracy. The writer has checked the strength of many such dichromate solutions by the titration of weighed sample of standard iron, and found the values by direct weight and by titration to be practically identical.

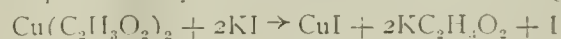
The calculation:



From the value of the thiosulphate solution, the value of the iodine is readily calculated.

Standardization Against Copper.—When a solution of sodium thiosulphate is to be used for copper determinations by the method of Low, it is well to obtain a copper value by direct titration against pure copper. The figure so obtained will be very slightly lower than that calculated from the thiosulphate standard as obtained by the above described methods.

When a solution of copper acetate reacts with an excess of potassium iodide, cuprous iodide is precipitated quantitatively and iodine liberated according to



and the liberated iodine is titrated by the thiosulphate solutions.

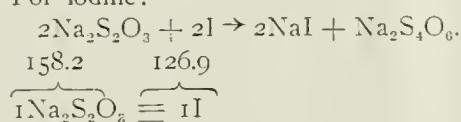
The procedure: 0.2 gm. of pure clean sheet copper is dissolved in the least quantity of 1:1 nitric acid (not over 5 cc.), and the nitrous fumes removed by boiling with a few cc. of bromine water. The solution is diluted to 50 cc., ammonia added to the formation of a clear blue solution, the excess of ammonia removed by boiling, and the solution cooled. Acetic acid is then added in slight excess, and, when the whole is perfectly cold, 2 grams of potassium iodide dissolved in a few cc. of water. The total bulk should be about 100 to 150 cc. The liberated iodine is then titrated to a light yellow color, starch added and the titration completed to the first discharge of the blue color. The blue will reappear in about half a minute, but the first end point must be taken. It is not advisable to run

over the end point with thiosulphate and titrate back with iodine. The end point is fugitive because the small amount of nitric acid set free by the acetic acid liberates some iodine from the potassium iodide, more thiosulphate is used, and the results in standardizing are low, or in the determination, high. This error, which is very small in the hands of an experienced operator, is practically eliminated when a direct copper standard is obtained.

Sodium thiosulphate solution is commonly used for the determination of:

Free iodine.
Free chlorine.
Free bromine.
Hypochlorites.
(Available chlorine in)

Peroxides.
Chlorates and perchlorates.
Chromium.
Lead (from lead chromate).
Ozone.
Iodine solution is used for:
Arsenic.
Antimony.
Sulphur (in iron and steel).
Sulphurous acid.
For iodine:

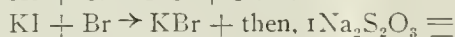


and the weight of thiosulphate per cc. $\times \frac{126.9}{158.2}$ gives the iodine value.

Wt. $\text{Na}_2\text{S}_2\text{O}_3$ per cc. $\times 0.8022 =$ iodine value.

For chlorine and bromine:

Since $\text{KI} + \text{Cl} \rightarrow \text{KCl} + \text{I}$ and



$1\text{Cl} \equiv 1\text{Br}$ and the chlorine value $= \text{Na}_2\text{S}_2\text{O}_3$ value $\times$
Cl

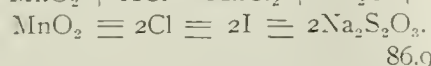
— and the bromine value $= \text{Na}_2\text{S}_2\text{O}_3$ value $\times$
 $\text{Na}_2\text{S}_2\text{O}_3$
 $\text{Br}/\text{Na}_2\text{S}_2\text{O}_3$.

$\text{Na}_2\text{S}_2\text{O}_3$ standard $\times 0.2241 =$ Cl value.

$\text{Na}_2\text{S}_2\text{O}_3$ standard $\times 0.5051 =$ Br value.

The chlorine standard so calculated answers for the standard for available chlorine in hypochlorites.

The values for the thiosulphate solution in terms of the other substances mentioned above are calculated in exactly the same manner from the following equations:



86.9

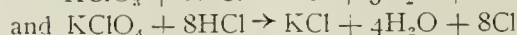
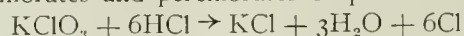
A unit weight of $\text{Na}_2\text{S}_2\text{O}_3 = \frac{158.2}{2} = 0.2747$ gm.

MnO_2 and the $\text{Na}_2\text{S}_2\text{O}_3$ standard $\times 0.2747 =$ the MnO_2

value. Similarly, for PbO_2 , since $\text{PbO}_2 + 4\text{HCl} \rightarrow \text{PbCl}_2 + 2\text{H}_2\text{O} + 2\text{Cl}$.

The $\text{Na}_2\text{S}_2\text{O}_3$ value $\times 0.7554 =$ the PbO_2 value.

For chlorates and perchlorates of potassium:



122.5

So the $\text{Na}_2\text{S}_2\text{O}_3$ value $\times \frac{122.5}{6(158.2)}$ or $0.1292 =$ the

138.5

KClO_3 value and the $\text{Na}_2\text{S}_2\text{O}_3$ value $\times \frac{138.5}{6(158.2)}$ or

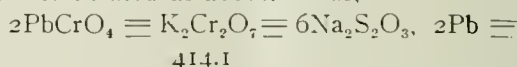
$0.1461 =$ the KClO_4 value. In the determination of chromium the chromium is oxidized to the condition of the chromate by alkaline oxidizing fusion or otherwise, and the chromate titrated exactly as in the standardization by means of potassium dichromate. In the reaction, $\text{K}_2\text{Cr}_2\text{O}_7 \equiv 6\text{I} \equiv 6\text{Na}_2\text{S}_2\text{O}_3$, and so $2\text{Cr} \equiv 6\text{Na}_2\text{S}_2\text{O}_3$.

104

The $\text{Na}_2\text{S}_2\text{O}_3$ value $\times \frac{104}{6(\text{Na}_2\text{S}_2\text{O}_3)}$ or $0.1096 =$ the

Cr value.

For lead, the lead is precipitated as PbCrO_4 and the chromate titrated as above. Thus,



414.1

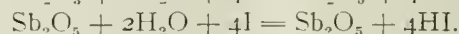
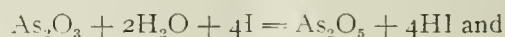
$6\text{Na}_2\text{S}_2\text{O}_3$, and $\frac{414.1}{6(158.2)}$ or $0.4367 \times$ the $\text{Na}_2\text{S}_2\text{O}_3$ value $=$ the lead value.

For ozone, the reaction is represented by the equation: $2\text{KI} + \text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{KOH} + 2\text{I} + \text{O}_2$. From this, $\text{O}_3 \equiv 2\text{I} \equiv 2\text{Na}_2\text{S}_2\text{O}_3$ and the $\text{Na}_2\text{S}_2\text{O}_3$ stand-

48

ard $\times \frac{48}{2(158.2)}$ or $0.1517 =$ the ozone value.

When the iodine solution is used for the determination of arsenic and antimony, the reactions are represented by:



So $\text{As} \equiv \text{Sb} \equiv 2\text{I}$.

74.95

The iodine value of the solution, then, $\times \frac{74.95}{2(126.9)}$ or $0.2953 =$ the arsenic value, and the iodide value

119.8

$\times \frac{119.8}{2(126.9)}$ or $0.4722 =$ the antimony standard.

In the determination of sulphur in iron and steel, the sulphur is evolved as H_2S , caught, set free, and titrated with iodine according to $\text{H}_2\text{S} + 2\text{I} \rightarrow 2\text{HI} + \text{S}$.

$\text{S} \equiv 2\text{I}$ so the sulphur value of the iodine solution

32

$=$ the iodine value $\times \frac{32}{2(126.9)}$ or 0.1263 .

The solution used for this determination should be of about fiftieth rather than tenth normal strength. It may be prepared from the deci-normal solution by exact dilution in the ratio of 1 to 5.

To summarize:

For sodium thiosulphate solutions

The $\text{Na}_2\text{S}_2\text{O}_3$ value $\times 0.8022$ = the iodine value.

The $\text{Na}_2\text{S}_2\text{O}_3$ value $\times 0.2241$ = the chlorine value.

The $\text{Na}_2\text{S}_2\text{O}_3$ value $\times 0.5051$ = the bromine value.

The $\text{Na}_2\text{S}_2\text{O}_3$ value $\times 0.2747$ = the MnO_2 value.

The $\text{Na}_2\text{S}_2\text{O}_3$ value $\times 0.1292$ = the KClO_3 value.

The $\text{Na}_2\text{S}_2\text{O}_3$ value $\times 0.1461$ = the KClO_3 value.

The $\text{Na}_2\text{S}_2\text{O}_3$ value $\times 0.1096$ = the chromium value.

The $\text{Na}_2\text{S}_2\text{O}_3$ value $\times 0.4367$ = the lead value.

The $\text{Na}_2\text{S}_2\text{O}_3$ value $\times 0.1517$ = the ozone value.

For iodine solutions,

The iodine value $\times 1.2465$ = the thiosulphate value.

The iodine value $\times 0.2953$ = the arsenic value.

The iodine value $\times 0.4722$ = the antimony value.

The iodine value $\times 0.1263$ = the sulphur value.

IMPORTS OF SOAP IN CHINA.

The U. S. Consul at Hongkong report that the increased use of soap and foreign soap materials in China which has been developing for several years has been such that the manufacture of soap in China along modern lines and with materials usual in foreign countries is developing rapidly. In Hongkong there is a soap factory whose capacity has increased greatly in the past three years and further development is anticipated, while in the Yangtze Valley the consumption of soap has come to such development that British soap manufacturers are establishing an immense soap manufactory in Shanghai. The imports of soap of all kinds into China in 1912 were valued at \$1,730,725 gold as compared with value of \$1,470,542 in 1911 and \$1,273,669 in 1910, and the imports in 1913, according to preliminary figures, show a similar increase over the previous year. At several ports in the vicinity of Hongkong imports have more than doubled in the past three years. About half of these imports come from Great Britain direct, in addition to considerable quantities of British soap imported through Hongkong. Japan is the next on the list of countries furnishing the supply, with Austria and Germany following. Soap imported from the United States is comparatively small in amount and the supply is confined largely to the fine trade.

The imports of soap into Hongkong per annum apparently average about half a million dollars, no reliable figures being available as to the exact imports. Considerable quantities are consumed locally by the Chinese population as well as by other residents, and well toward a quarter of a million dollars' worth of the product is exported to China, the Chinese customs figures for 1912 showing imports of soap from Hongkong to the value of \$238,306 gold. Much of these imports consist of the product of the Hongkong fac-

tory, which, in fact, is supplanting foreign soap in the markets of the interior. The Hongkong factory is now producing considerable quantities of salt-water soap, of blue mottled soap, and several grades of laundry soap, including a cheap grade of soft soap. The oils used come almost entirely from the cocoanut oil mill now in operation at Manila, the soda ash comes from Germany and Great Britain, and rosin from the United States. There has been a marked increase in the use of better grade soaps in the past three years, though the great mass of the product used at present is of the cheaper qualities. Most of the soap imported and manufactured and exported is handled in long bars packed in 50 and 75-pound cases, the former size being the more general.

All records in coke production were broken in 1913, according to a statement by Edward W. Parker, of the United States Geological Survey, the output being 46,311,369 short tons, valued at \$128,951,430. This is an increase over the 1912 output of 2,327,770 tons in quantity and \$17,146,317 in value. Of the 1913 production 33,596,669 tons was made in beehive ovens and 12,714,700 tons, or 27.4 per cent, in retort or distillation ovens where all the by-products—tar, gas, ammonia, etc.—are saved. The increase in production of by-product coke was over twice as large as the increase in beehive coke. The principal increase in by-product coke production in 1913 was in Alabama, where the gain was nearly 50 per cent, from 1,349,797 tons in 1912 to 2,022,959 in 1913. The increase in Pennsylvania was nearly one-third, from 1,974,619 tons in 1912 to 2,628,680 tons in 1913. Indiana showed an increase of 110,686 tons, and Illinois of 94,609 tons. A large part of the coal used in by-product ovens in states that do not produce coking coal was obtained from West Virginia mines. Mr. Parker estimates that the quantity of West Virginia coal made into coke outside of the state was 7,800,000 tons. The quantity of coal made into coke in West Virginia was 4,034,251 tons and the quantity of coke produced therefrom was 2,472,752 tons. If all the coke made from West Virginia coal were credited to that state it would amount to about 7,750,000 tons.

Returns covering the operations of the Norwegian electrochemical companies during 1913 would indicate that the industry there is now established on a very sound basis. The companies operating worked full time throughout the year. The exports of Norwegian saltpeter amounted to 70,171 tons in 1913, as against 51,701 tons in 1912. The exports of nitrate of soda and nitrate of ammonia during 1913 were 17,028 tons, as compared with 13,480 tons in 1912. The production of calcium cyanamid in 1913 was 45,000 tons. The Norsk Act. Elektrokemist Industri has announced that its capital will be increased and that products not heretofore manufactured will be produced.

METALLURGY.

THREE DECADES' ADVANCE IN AMERICAN BLAST FURNACE CONSTRUCTION.*

By HERMAN A. BRASSERT.†

The manufacturer who, in the swift march of progress and in the pursuit of an industry, the foundation of which is ever changing with altering raw materials, does not constantly take stock of his equipment and rejuvenate it to suit the times, will soon find himself outclassed by his competitors.

With the variety of possibilities which present themselves in the operation of furnace plants, many forms of construction can be worked out and many can be made successful. But every improvement should be inspired by one common aim, and that is to facilitate the utmost uniformity of practice in order to gain the highest quality of product and the greatest possible economy.

For the sake of uniformity and to eliminate the danger of mixing various grades and the necessity of frequent burden changes, adequate space and equipment for the stocking of ores should be provided. This feature will allow of a greater latitude in selecting the most suitable furnace burden at a given time. If a cargo can be spread evenly over a large pile, so that any cross section of it represents a true average of all cargoes received during a shipping season, the furnace will receive the ores in the most uniform shape.

The bins should be so designed that the ore can be easily withdrawn under perfect control on the part of the operator. With sufficient slope and closely spaced gates to prevent the sticking of the ores in the corners, proper movement of the entire contents can be secured. Furnace troubles are always more frequent in winter than in summer, due to the difficulty of correct charging when the materials are frozen. In cold climates, therefore, the charging floor should be enclosed and the bins heated, preferably by waste gases.

In handling the coke, the main object should be to avoid abrasion. That charging system is preferable which transfers the coke from the ovens or railroad cars into the furnace with the least number of drops. The coke can be charged by volume or by weight. The former method is independent of varying moistures in the coke, and automatically compensates for certain variations in quality, by delivering a greater weight of smaller, denser coke. This regulation, however, is not always correct, since smaller coke is not propor-

tionately inferior, but it tends to equalize the error. Where the coke is uniform in moisture and furnace value, the weighing method will give excellent results.

The coke pockets should be made of ample capacity to avoid delays, and should be designed to keep all of the contents in motion and to avoid the accumulation of fines—a most frequent cause of furnace troubles. The dust should be eliminated by screens placed in the bin or at the gates.

The charging or larry car should preferably be large enough to hold a full charge of ore and stone. This saves labor and wear by decreasing the number of trips, and allows the furnace to be kept full with the least effort, even when driving fast, at the same time rendering the percentage of error in weighing smaller.

The ship hoist can be either of the single or the double type. The latter has the advantage of filling the furnace faster, but brings with it the difficulty of obtaining an even distribution between the right and left side of the furnace, which must be overcome by proper construction of the top. Materials dumped from an overturning skip bucket will arrange themselves more or less according to size, the coarse particles falling the furthest and the fines remaining behind. In order to avoid uneven distribution of fine and coarse materials, the design of the skip bucket, receiving hopper and top should be carefully worked out; as should also the range of skip travel and the speed of dumping, which should be under positively fixed control. The single skip allows the use of a cylindrical bucket with bottom discharged, dumping centrally over the bell and giving a correct distribution on the top of the furnace. But with that design it is necessary to correct the distribution in the bucket itself with regard to coarse and fine materials. This is a difficult matter and can only be accomplished by rotating the buckets. This type of hoist, however, has the decided advantage of more carefully handling the coke charges, and for that reason has been largely adopted in Europe.

The blast furnace top itself has been the subject of more variations in design than any part of the furnace. Besides being a gas seal, it has to fulfill the important function of proper stock distribution. It is difficult to accomplish this with a stationary top, and many furnace men prefer to abandon it in favor of rotating mechanical tops. Whatever type of top is selected, it must be borne in mind that a breakdown generally necessitates stopping the furnace; therefore the construction should be simple and strong. If a good distribution can be obtained without resorting to the complication of rotary mechanism, all the better. If

*From a paper presented at the Spring meeting of the American Iron & Steel Institute, New York, May 22.

†Superintendent of Blast Furnaces, Illinois Steel Co., South Chicago, Ill.

deemed necessary to employ a rotating top, such a design should be selected which will give a satisfactory distribution, even if it should cease to rotate.

Many of the irregularities of stock distribution bear no relation to the design of the top; as for instance, the building up of ore on the big bell, which with Lake ores cannot be altogether prevented, even with the modern steep angles, and requires constant watchfulness or the shifting of the furnace top relative to the furnace center caused by expansion and contraction, or the warping of the bell and hopper and the uneven wear of the stock-line. Neither can irregularities of charging—such as are caused by lack of care on the part of operator, severe weather, and many other causes—be corrected by any design of top. It will be seen, therefore that a rotating top is by no means the

ly by special stock deflectors. In European practice the stock column is much more open, less fines and considerable lump ores still being used with large sized coke and stone. Under these conditions this charging method seems to give satisfaction; and in many places it is still adhered to, in spite of the great complication of design especially when combining the central gas off-take with a mechanical top.

Under our conditions, using practically none but fine ores, in order to obtain uniform practice, the principal aim must be to prevent the channelling of gases. As it is their natural tendency to follow the walls where the stock is continually loosened by friction, we deposit the ores next to the wall, thus forcing the gases to the center. In order to accomplish this we use a method opposite to the one described lowering a

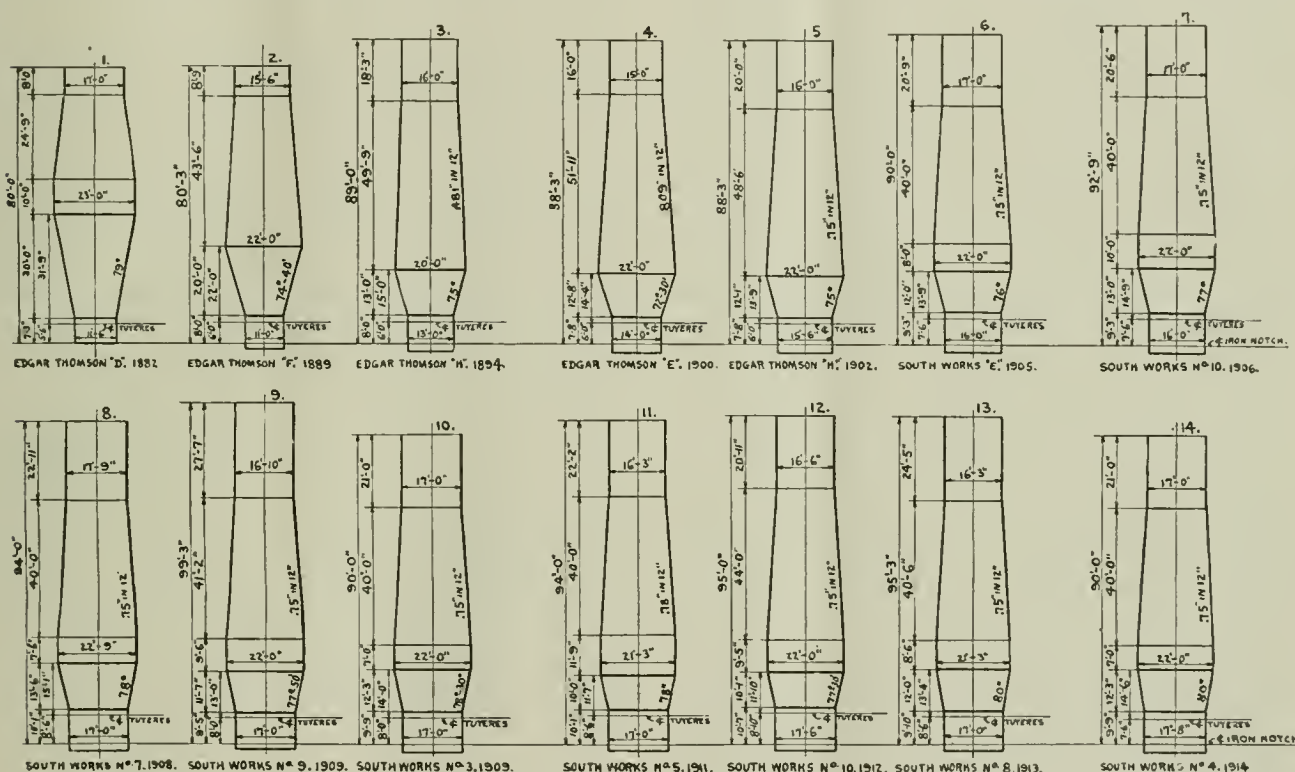


Diagram Showing Various Types of American Blast Furnaces.

cure of all evils. Careful supervision, constant vigilance, or regular and frequent inspection, are the only safeguards and should be practiced regardless of the type of top in use.

With a uniform distribution on the big bell, the next question is how the charges should best be arranged in the stock column. There are two opposite methods of depositing the materials in the furnace. The one, which is used abroad, but not in this country, consists in raising a cylindrical bell and allowing the charge to glide off the hopper towards the center of the furnace, there forming a cone with an apex of fines and a base of coarse materials, which gives the gases a tendency to ascend next to the walls. This is counteracted by using a comparatively small hearth with tuyers projecting far in, or a central gas off-take, and frequent

large conical bell and dumping the charges against the furnace fall, the finer materials remaining there on a higher ridge, the coarser ones rebounding and rolling toward the center. This opens up the stock column in the center and serves the same purpose as a central gas off-take, only in a milder form. A recent experiment made at South Works with a central tube, showed conclusively that this arrangement is too radical for Mesaba ores.

For the opposite purpose, that of loosening the stock next to the wall, various modifications of the plain bell have been tried. Such attempts originated in the early days of Mesaba practice, when it was thought that the formation of scaffolds could be avoided by placing less fines next to the wall. Designs of this kind have mostly been abandoned, as it

was soon found that the evil of gases channeling along the walls and unreduced ores descending in the center, with high fuel consumption and buckshot iron as the result, was too high a price to pay for keeping walls clean. The plain bell with the gas off-takes at the periphery of the stack is evidently the best and by far the simplest design under our present conditions of raw materials. The problem to obtain a free working furnace on Mesaba ores could, however, not be solved until the correct furnace lines were established.

Going back in history, when Mr. Gayley, in 1890, read his memorable paper on the development of American blast furnaces before the British Iron and Steel Institute, he outlined the trend of improvements in his concluding remarks by stating that in the last decade there had been three steps. First, in 1880, the introduction of rapid driving, with large outputs and high fuel consumption; second, in 1885, the production of an equally large amount of iron with a low fuel consumption, by slow driving; and third, in 1890, the production of nearly double that quantity of iron, on a low fuel consumption, through rapid driving. Mr. Gayley himself, who was then in charge of the Edgar Thomson furnaces, was largely responsible for this progress. Much credit also belongs to the management of the Illinois Steel Company, who on their Union and South Chicago furnaces made the best yearly fuel records of that period.

In the early eighties the linings at the Edgar Thomson furnaces had boshes half way up the stack; as, for instance, furnace "D," shown in Fig. 1 in the attached chart of furnace lines. The construction was taken over from the charcoal and anthracite practice with hard ores. It was realized that with coke as a fuel and with softer ores, much more rapid driving was not only possible, but highly desirable, if it could be done without an increase in fuel. The furnace lines were conformed to this idea and the boshes lowered from 30 feet to 20 feet, in the period covered by Mr. Gayley's paper. A furnace of this type is illustrated in Fig. 2, showing furnace "F" at Edgar Thomson in 1889. By the rapid yet consistent development of furnace lines and practice in this direction, and by strengthening his blowing equipment accordingly, Mr. Gayley was himself able in a few years to surpass the prediction made in his paper. By 1894 the output of these furnaces had been increased to an average of 400 tons per day with a coke consumption of less than 1,900 pounds. This was accomplished by raising the stack from 80 feet to 90 feet, lowering the bosh to 15 feet, increasing the size of the hearth to 13 feet, thus maintaining the previously established 75-degree bosh angle. A furnace of that type is shown in Fig. 3, giving Edgar Thomson furnace "H" in 1894.

A few years later Mesaba ores entered into the problem. In lowering the bosh and raising the furnace to 90 feet, still maintaining the 16-foot stock-line, the angle of the inwall had become steeper (see Fig.

3), and this had the tendency to retard the descent of the charges. The next step taken, therefore, was to increase the batter in the stack, which could be accomplished by narrowing the stock-line and lengthening the straight top section, or by widening the bosh. At the same time the advantage of still lower boshes was realized. These two developments together resulted in the type of furnace shown in Fig. 4 giving the lines of furnace "E" at Edgar Thomson in 1900. Furnaces of this type were able to produce 500 tons of iron per day on a burden of one-third Mesaba ores, but it was difficult to maintain uniform practice owing to accumulation of stock on the flatter bosh. This suggested the return to the 75-degree bosh angle by the use of still larger hearths, a step which was not taken without hesitation, as we feared an insufficient penetration. But no difficulty of that kind was experienced, and furnaces of this type marked quite an improvement, by establishing the average yearly output of 500 tons per day on 50 per cent of Mesaba ores with uniform practice. Such a furnace is illustrated in Fig. 5, giving Edgar Thomson furnace "K", built in 1902, which in 1903 averaged 539 tons of ore on 1,985 pounds of coke. I have given the Edgar Thomson furnaces as an example, as they were representative of this development and, together with the Duquesne furnaces, established the best blast furnace records of that period.

Similar lines, consisting of a 16-foot stock-line, $\frac{3}{4}$ inch to the foot batter of the inwall, a 22-foot bosh, 14-foot six-inch to 15-foot six-inch hearth diameter and a 75-degree bosh angle, were quite generally adopted on 90 and 100-foot furnaces using Mesaba ores. The percentage of these ores in the burden was gradually increased up to 70 per cent in the next five years, but not without a distinct increase in coke consumption, as shown by the following figures representing the averages of a large number of American furnace plants using like ores:

Year.	Per cent Mesaba.	Lbs. coke.
1902.....	43.8	2,155
1903.....	50.3	2,191
1904.....	55.0	2,239
1905.....	61.0	2,275
1906.....	65.2	2,343
1907.....	68.7	2,362

The first experience with these ores had clearly shown that on account of their reducibility, they could be smelted rapidly and with a low fuel consumption, providing the furnace could be made to work uniformly, and the walls could be kept clean. The more regular, faster movement of the stock—by offering less opportunity for the gas to channel, and a more intimate contact and better heat exchange between ores and gases—allows a heavy burden to be carried in spite of the faster driving. The zone where the materials become plastic is kept at a uniformly low level, and there is less danger of scaffolds forming above the bosh. The task, therefore, is to design a furnace in such a way that the least resistance is

offered to the free travel of the stock. With the proper batter already established, the chief impediment remains the bosh. As the melting zone is lowered, the bosh must follow, otherwise the materials will strike the inverted angle before the proper shrinkage through fusion takes place, causing the furnace to hang. Furthermore, a steeper angle should facilitate the stock movement in the bosh, and should, in conjunction with an increased hearth diameter, tend to keep the materials loose in arriving at the tuyere zone, allowing a free penetration by the blast and preventing high blast pressures. These ideas were embodied in successive linings of the furnace at South Works by increasing the hearth diameter up to 17 ft. 8 ins., decreasing the height of the bosh above the tuyeres below 12 ft., and steepening the bosh angle to 80 degrees, a development which is clearly shown by Figs. 8-14 on the table of furnace lines.

In the latest models of these furnaces the bosh is no longer a conspicuous part. The old theory, which attributed to the bosh the function of carrying the weight of the burden, and of narrowing the hearth to the point of proper penetration, must now be modified. The bosh seemingly has but one important duty—that of retarding the melting ores, so they will not run ahead of the coke and darken the tuyeres by reaching them before being properly prepared. There is nothing to indicate that we have reached the limit in low and steep boshes, simply by further widening the hearths and without resorting to such means as the elliptical furnace.

The hearth diameter, and not the bosh diameter, must today be recognized as the determining factor in influencing the rate of output. In designing new lines, the hearth dimensions should be established first, according to the desired production. By adding a bosh of correct height and angle, the bosh diameter automatically results.

Stacks of different heights are in operation at the South Works. Whereas laboratory tests show that Mesaba ores can be completely reduced in a few hours by furnace gases at suitable temperatures, actual conditions are different. Practical experience proved that even with these easily reduced ores it takes considerable time, first, to thoroughly preheat every particle in a large bulk of ore, and then to bring it into contact with the volume of gases required to complete reduction. This led to a gradual increase in the height of stacks as the output was increased. Experience seems to show quite clearly that, for Mesaba ores, the proper height is 90 feet.

A greater height of the stack than that necessary to accomplish the desired reduction is not only useless, but detrimental by extending the zone where the coke is attacked by CO_2 , and unnecessarily increasing the blast pressure. Furnaces which are too low compared to their hearth diameter have too low a blast pressure to give a proper penetration in the combustion zone, if driven at the rate most suitable for economical re-

duction. If higher blast pressure and better penetration are obtained by increased wind volume, the zone of fusion rises and the time available for pre-heating and reducing the ore charges becomes too short, resulting in an excessive proportion of "direct" reduction by solid carbon. Furnaces operated in this manner are able to produce as large or larger tonnage than similar stacks of greater height, but will invariably show a higher fuel consumption. The practice of carrying the stock-line at a lower level has the same effect—the tonnage is increased at the expense of fuel consumption, except where the furnaces are too high, in which event they should be cut down rather than jeopardize uniform distribution and life of lining.

The diameter of the stock-line should be carefully chosen to correspond with the hearth and the prospective volume of wind. It should not be appreciably smaller than the hearth, otherwise the dust loss when using fine ores will be excessive. Neither should it be materially larger, as it would be difficult to attain the desired batter of the inwall without extending the cylindrical top section too far down, or inserting too high a cylindrical section above the bosh, both of which are liable to interfere with the smooth travel of the stock. The stock-line approximately determines the size of the bell. With Mesaba ores a bell of from three to five feet smaller diameter than the stock-line has given the best results. The method of charging has some influence on this relation.

The number of tuyeres, if kept within certain limits in proportion to the size of the hearth, is of little importance, since not their number but their combined free area determines the degree of penetration with a given wind volume. At the South Works 10 and 12 tuyeres are used with equally good results on the largest hearths.

The relative position of the tuyere level, cinder notch and tapping hole deserve the most careful study. By increasing the height of the tuyeres above the cinder notch, a larger amount of slag can be held and the clogging of the tuyere zone with slag, which interferes with the combustion, is prevented. The greater the distance between cinder and iron notch levels, the smaller the danger of the iron reaching the cinder notch and causing damage. With a fixed hearth diameter, this distance determines the maximum weight of individual casts. However, it cannot be increased except in proportion to enlarged output, otherwise the bath of iron, removed too far from the active tuyere level and held too long in the furnace, will cool and cause those manifold troubles due to physically cold iron, which affect furnace and steel works practice alike.

Since the character of the ores is changing all over the world, much in the same direction as in this country, the development of furnace lines in other countries will in all probability be similar.

Having established suitable lines, the next problem is to maintain them. Nothing contributes so much to the long life of a lining as a low fuel consumption and uniform practice. The hearth and bosh, which in the early days usually determined the length of a campaign by giving way first, are on our modern furnaces so efficiently cooled and so strongly armored that they outlast the lining in the stack. The ability to maintain the bosh indefinitely, by the insertion of cooling plates, led to many attempts to follow the same construction in the inwall. But the plates caused the lining to become corrugated between rows and to wear back above the top row, forming shelves highly inducive to scaffold formation. Furthermore, it was not an easy matter to so arrange the plates that they could be exchanged when leaking. Cooling plates above the mantle have only survived where they are placed from 18 to 22 inches back of the face of the inwall, and in this position they have not much effect in preserving the original lines. These difficulties led to the construction of thin lined furnaces on both sides of the water, from nine inches and 13 inches of brick work in this country, and from three inches to a mere coating of clay used on a few German furnaces. Very thin linings have only proved advantageous for making special grades of iron or when using coarser burdens. With Mesaba ores it is impossible to prevent the fine materials from building up on the cold shell, after the lining is worn away.

Therefore the life of a thin lining is determined by the life of the brick work itself, and this is too short in the case of a nine-inch or 13½-inch lining to make this construction profitable.

Excessive thickness of a lining has no advantage, since before it wears out, the lines become so irregular that economical practice is impossible. From 22½ to 36-in. seems, therefore, the proper thickness. A good lining, if allowed to become properly seasoned and coated will wear slowly and uniformly, providing the stock and blast distribution is correct. A stack lined with a moderately thick lining does not require water cooling, but when the brick work does wear, the campaign can be prolonged by the application of water sprays without much deviation from the original lines.

The quality of the fire brick is the next important item in prolonging the life of a lining. The hearth and bosh brick are protected by efficient cooling; the top brick generally by wearing plates. The problem is to obtain brick for the lower inwall which will last without protection. Here they are exposed simultaneously to abrasion and high temperatures. They must, therefore, have a high melting point and yet be hard and tough. The quality of clays and their treatment, as well as the various methods of brick manufacture, enter here. Machine-pressed brick are especially well adapted to meet the requirements of a good inwall, and owing to their correct shapes can be laid with narrower joints. They have given excellent re-

sults at the South Works during the past five years, from 600,000 to 800,000 tons of iron being obtained on a lining, and with good practice to the end. In Germany carbon brick are frequently used in the hearth and bosh, with varying results and opinions widely differing as to their value.

A great variety of wearing plates have been designed to protect the stock-line, but very few have proved successful. The plates should be made in small enough sections and of such metal and design that they will neither crack nor warp. To prevent their working loose and interfering with the distribution, they should be tied in with the brick work. Some furnace men prefer to avoid the complication of such arrangement by repairing the brick work at the stock-line during the campaign.

The strong, riveted, steel plate shell surrounding the brick work is one of the best features of our construction. It is now made so heavy that the lining can be laid quite close against it, insuring tight joints, which are forced to close with the expansion of brick work. The shell may serve the purpose of supporting the top ring, hopper and down-comer pipes; but the skip hoist and dumping mechanism should under no circumstances be attached to it. These must be supported independently to avoid shifting with the expansion of the furnace. The furnace shell protects the brick work and allows weak spots in the lining to be held for long periods by the application of water sprays. In Germany furnace shells are found only exceptionally and on older furnaces. The construction commonly used there encircles the brick work with steel bands.

Many stacks are cooled, sometimes up to the top, by open cast iron water boxes which are placed between the bands and generally extend to within a few inches of the interior face of the lining. For this construction is claimed the advantage of accessibility when repairs to the brick work are needed. In some instances German stacks have been practically relined without blowing out, by banking below the mantle. The furnace with a steel shell is certainly stronger and safer, and can be kept in blast under conditions which would force an open furnace out of operation. Our practice would seem to prohibit the German construction on account of high blast pressure, loss of gas, and danger of ruptures in case of heavy slips. In the bosh where we employ the German stack construction, they often use a steel jacket, similar to the one employed in this country on astern furnaces using magnetites and imported ores. With Mesaba ores the more intense cooling of the water-sprayed jacket causes accumulations to form on the bosh, which periodically melt down, making the practice very irregular.

The gas off-takes should be located as high above the stock-line as possible, out of the path of the falling stock. There should be several, preferably four and their area should be sufficient to prevent exces-

sive velocity. In this manner, and by turning these off-takes upward before they lead down to the dust catcher, the amount of flue dust and fine coke carried over has been decidedly reduced. One or more good safety bleeder valves should be provided, so designed that they will give ample relief during heavier slips without allowing any coarse materials to be thrown out.

The dry gas cleaning system need only consist of one dust catcher of good size and an efficient centrifugal cleaner. These will eliminate practically as much dust as more elaborate arrangements, and are economical in construction and operation. A primary gas washing plant of sufficient capacity to wash all the gas for stoves and boilers should form part of every modern furnace plant. There is no question as to the value of washed gas for stoves, and a proper design of boiler settings, to allow of a free development of the flame and complete combustion before the gases strike the colder surfaces, will render it economical for boilers also.

With washed gas the problem of stove construction becomes comparatively easy. Small checkers can be employed and thereby the heating surface is increased sufficiently so that four large stoves will furnish all the heat required. With clean gas these can be kept in continuous service. They form a simpler layout and are preferable to five smaller stoves on account of better heat economy, less radiation surface and fewer valves.

The latest innovations, which come to us from Germany, claim to increase the capacity and efficiency of existing stoves by using compressed air for combustion, or by installing heat interchangers in the chimney flue for pre-heating the air.

When using fine ores, strong blowing equipment is essential to insure the delivery of a uniform amount of wind, even under conditions of high blast pressure. Gas engines of good design and liberal dimensions have proven to be especially adapted for this service, since the cost of blowing is but little affected by high blast pressures, whereas it can be made almost prohibitive in the case of steam engines in districts of high cost of fuel. The great economy of the gas-blowing engines has been a long established fact. Practice in recent years has proved their reliability in service, and has thereby definitely decided in their favor against reciprocating steam-blowing engines, except in a few localities favored by very low coal prices or at isolated furnace plants where the surplus gas is not utilized, and therefore has no value. With the gradually increasing cost of coal mining and the growing tendency to make economical use of the surplus gas, the gas engine will continue to enlarge its field of usefulness. The steam turbo blower may conquer a position in the localities least favorable to gas engines, owing to its low cost of installation, small space requirement and simple operation. However, practice has not yet definitely proved that it will

deliver as constant a supply of air as the reciprocating engine, particularly when fine ores are used, and the resistance in the furnace is subject to considerable and sudden variations.

In every art and industry the living generation, having reached a certain goal, is prone to believe that no further progress is possible. At the present time, with furnaces producing 500 tons and more daily from difficult ore mixtures, with fuel consumptions which we think closely approach the low limit, we may not see our way clear to further improvement; yet the possibilities are now as great as ever. Perhaps they lie in another direction, and we need not be discouraged if we fail to develop the 1,000-ton furnace or are unable to lower our past fuel records.

Our problem, I am convinced, is to reclaim and put to use those vast bodies of ore and coal which, owing to their adverse character, have in the past not been available for the manufacture of iron. This is by far our greatest task, a task which has the highest economic value in substantially contributing to our country's wealth.

The magnitude of the unit with which we deal, the large responsibilities involved, the long period of time which must elapse before new ideas are approved by practice or condemned, the many disappointments with which all of us have met, are bound to make us cautious and conservative. Yet in this age, where science and engineering have put at our command resources undreamed of by our predecessors, we will, I trust, in the daily drudgery of making pig iron, keep sight of our wonderful opportunities and do our share in advancing the blast furnace art.

The U. S. Consul at Vienna, Austria, reports that numerous advantages over pipes of other materials are claimed for the asphalt-paper pipes that are being introduced in Austria. Originally the paper pipes were employed for electric-cable conduits, but other uses have now been found for them, and the makers assert they can replace iron, steel, copper, and clay piping for all purposes except the conveyance of hot fluids, concentrated acids, and petroleum products. The pipes are made from a special kind of asphalt paper of German manufacture (the paper made in Austria not being wide enough), are exceedingly light in weight compared with metallic or clay piping, and, in addition, are flexible to a slight degree. They are not affected by sudden changes of temperature, nor do the stray currents of electric-tramway systems cause electrolysis of buried mains. The patents covering the process and the machinery for making the pipes are owned by the Anglo-Austrian Bank of Vienna; application has been made for American patents on both. Up to this time no machine-made pipes have been produced, as the machinery has only recently been perfected. A small sample of hand-made pipe will be loaned to interested American firms by the Bureau of Foreign and Domestic Commerce, Washington.

SECONDARY METALS, 1913.

The value of the "secondary metals," exclusive of gold, silver, platinum, and iron, recovered in the United States in 1913, was \$72,845,000, according to J. P. Dunlop, of the United States Geological Survey. Even this large figure is a decrease compared with 1912, when the value was \$77,396,000.

"Secondary metals" are those recovered from scrap metal, sweepings, skimmings, drosses, etc., and are so called to distinguish them from the metals derived from ore, which are termed "primary metals." The distinction does not imply that secondary metals are of inferior quality. The reports to the Survey do not include the very large quantity of old iron and steel remelted, neither do they include the precious metals. In fact, while the data given in this statement cover a large field and form an essential addition to the reports on primary metals, the scope of the inquiry made by the Survey reveals only in a partial way the vast extent of the waste trade industry, which yearly becomes greater and better organized. The value of iron and steel reused probably exceeds that of remelted brass, and the value of the old rubber and paper stock utilized amounts annually to many millions of dollars.

The Survey's inquiry was extended in 1913 to cover secondary aluminum and the result appears to have justified the extra effort. The values given for the secondary metals are arbitrary and are based on the approximate average value of the primary metal for the year. While the junk dealer buys small and scattered quantities of scrap metals at low prices which enable him to resell the material at a substantial profit regardless of the changing value of primary metal, the keen competition for large quantities of drosses and carefully sorted scrap metals results in good prices being paid for such waste materials. In fact, it appears that in 1913 the decline in metal prices and the slackened trade conditions, combined with sharp competition, raised comparative prices of scrap and drosses until the margin of the large jobbers, smelters, and refiners handling this material was too small to permit very profitable operation.

Although the quantity of reclaimed metal compared favorably with that of former years, stocks of metal derived from scrap and drosses were much larger at the end of 1913 than in 1912. After remelting or refining, these secondary metals, selling at only slightly lower prices than new metal, displace an equivalent quantity of primary metals and must be considered in any estimate of stocks available for consumption in any year. For a few purposes requiring especial purity of material, it is necessary to employ primary or virgin pig metal, but as a general rule secondary metals can be used in whole or in part. In fact, most foundries, in order to compete for business successfully, must and do use secondary material, at least in part, and hence they purchase scrap metal and remelt it with primary pig metal or with composition ingot. The

secondary smelters, by handling large quantities of all kinds of scrap, are able to classify their material so as to produce continuously alloy metals of uniform composition suitable for use in work of different classes. Such composition ingots are being purchased and used in increasing quantities by many foundries and other manufacturers in place of primary metals or mixtures of new and scrap metals. It is asserted that the use of properly made and suitable composition ingot is more economical and produces better and more uniform products than the use of virgin metals or of mixed scrap and virgin metals in making alloys.

It has so far proved impossible to separate the statistics for secondary metal recovered from clean scrap made in the ordinary course of manufacture from the statistics of metal recovered from drosses and ashes and from scrap or old metal that had entered the trade as manufactured articles and been discarded. An estimate of the clean copper and brass scrap on the basis of replies from the larger secondary smelters and refiners, but no classification made by many of the dealers or smelters is available.

The use of magnetic separators to free scrap from iron, the recovery of metal from cinders and molding sand, and the use of machines to briquet small scrap in order to reduce the losses in melting continued to increase. Dealers and jobbers in scrap metal realize the necessity of combining to insure better grading of waste metals and more efficient methods of packing in order to obtain lower shipping rates. The large smelters and refiners of waste metals and drosses, many of whom conduct a business amounting to millions of dollars yearly, recognize the importance of proper separation and grading of metal wastes and of selling alloys of guaranteed composition, but the smaller manufacturers and metal buyers have not been as careful as they might have been in view of the undoubted fact that the larger portion of all waste material is collected by junk men and jobbers, who resell the material to the smelters, refiners, or manufacturers. The use of old metals has extended rapidly, and any co-operation that will remedy trade objections to the use of secondary metals in any branch of manufacturing, as well as any saving that lowers the cost of treating waste products, must result in a broader market and prices more nearly approaching those for virgin metal.

It is impracticable to segregate the statistics relating to the refining, remelting, and reuse of secondary metals according to states, but over 90 per cent of the refining and smelting of drosses and scrap metals in the United States is confined to the territory east of St. Louis and north of Ohio River. Reports were made by approximately 550 users of secondary material, of which about 150 were in Pennsylvania and West Virginia, 130 in New York, New Jersey, Connecticut, Maryland, and Massachusetts, and 150 in Ohio, Indiana, Illinois and Michigan. Over 60 per cent of the secondary aluminum was reported from the states of Ohio, Illinois, and Michigan. Smelters and

refiners in St. Louis, Chicago, Cincinnati, New York, and Philadelphia recovered over 80 per cent of the antimony in alloys. The larger portion of the secondary tin was refined by plants in Pennsylvania, New Jersey and New York. The recoveries of lead, zinc, and copper were more generally distributed. The greater number of the larger smelters or refiners of secondary metals are located at or near New York, Philadelphia, Pittsburgh, Tottenville (N. Y.), Chicago, Cincinnati, St. Louis, Detroit, and Cleveland, though there are many large plants at other places.

The total amount of secondary copper recovered in 1913, on the assumption that the brass remelted had an average copper content of 70 per cent, was 136,500 tons, of which 18,661 tons (about 4,000 tons more than in 1912) was recovered by plants refining primary metals and the remainder by plants treating only secondary materials. The copper produced by smelters of the latter class includes 36,716 tons of pig iron, 11,603 tons of copper in alloys other than brass, and 69,520 tons of copper in remelted brass. These figures indicate a decrease for 1913 of about 6,000 tons of pig copper, and 1,500 tons of copper in brass and an increase of about 2,300 tons in alloys other than brass. At least 45,000 tons was recovered from clean scrap made in the course of manufacture of copper and brass ware, so that only about 91,500 tons was obtained from ashes, cinders, and scrap, or from material that had actually been used and discarded. The value of the copper, both as metal and in alloys, is computed at the average yearly price quoted for casting copper by the "American Metal Market." According to the Bureau of Foreign and Domestic Commerce, the exports of scrap brass fit only for remanufacture, for the calendar year 1913, were 10,943 tons, and the imports were 3,395 tons. While many railways sell or turn in the larger portion of their brass and copper scrap and other metal waste to dealers in part payment for new material, the reports received show that the railways utilized in their own shops and foundries over 12,670 tons of brass, in addition to 900 tons of copper and 2,828 tons of copper in alloys other than brass.

The production of copper from secondary sources in 1913 was equal to about 17 per cent of the refinery output of primary copper in the United States from all sources, or about 22.4 per cent of the primary copper smelted from domestic ore.

The secondary lead recovered in 1913 amounted to 72,834 tons or about 5,700 tons more than in 1912. The secondary lead recovered as pig lead increased about 2,800 tons, a normal increase in view of the fact that the average lead price was nearly the same in 1912 and 1913. The recovery of lead in alloys increased 2,900 tons compared with 1912. The increase of 2,800 tons of pig lead from secondary material was due wholly to the increased recoveries made by those regular smelters whose product is mainly primary metal. The increase reported to the Survey in the quantity of lead in alloys, much of which is derived from remelted

babbitt and bearing metals, was doubtless due in part to a more careful canvass of the scrap-metal dealers, who not only act as brokers and middlemen but frequently remelt and sell babbitt, lead pipe, and spelter. Other important sources of secondary lead were old pipe, lead linings of acid tanks, and drosses from white-metal alloys. Regular smelters reported the recovery of 9,238 tons of lead from lead and antimonial lead scrap. The total output of secondary lead was equal to 15.2 per cent of the refined lead produced in the United States in 1913, compared with 13.5 per cent in 1912, or to 16.7 per cent of the refined lead produced from domestic ores in 1913. It was exceeded by the domestic lead output of only two states, Missouri and Idaho, and only one other state, Utah, had an output of lead nearly as large as the secondary lead recoveries.

The output of secondary zinc (including that in brass) amounted to 79,570 tons and equaled 23 per cent of the total production of primary spelter in the United States in 1913, compared with 24.1 per cent in 1912. The zinc recovered in alloys other than brass amounted to 3,743 tons, compared with 3,912 tons in 1912. Of the 50,005 tons of secondary zinc recovered as spelter, 25,991 tons was obtained by redistillation from drosses, skimmings, etc. In addition to the large quantity of spelter recovered, it is estimated that over 15,000 tons of zinc chloride was made from drosses, skimmings, etc., and likewise several thousand tons of zinc pigment lithopone.

The quantity of spelter recovered by redistilling drosses, skimmings, etc., was about the same in the years 1912 and 1913. Two zinc smelters in New Jersey and Pennsylvania which recover spelter entirely from drosses, skimmings, etc., used large 800 or 1,000 pound retorts instead of the small ones used by smelters treating ore or mixed ore and drosses. A large portion of the secondary spelter recovered was reported to be of high grade, ranging above 99 per cent pure and equal in practically every respect to the spelter made from ore. The quantity of secondary spelter produced by smelters having an output derived mainly from ores increased about 1,800 tons. This would apparently indicate that the practice of mixing zinc concentrates and drosses is extending. Although prices of spelter were much lower in 1913 than in 1912, the exports of zinc dross amounted to only 28 tons, compared with 205 tons in 1912 and 4,246 tons in 1911.

The production of secondary antimony, of which all but 45 tons was recovered in alloys, increased from 2,506 short tons in 1912 to 2,705 tons in 1913. The value given is arbitrary and is based on the average yearly price for Cookson's antimony given by the "American Metal Market." The only antimony ore of domestic origin smelted in the United States in 1913 was 116 tons from Nevada, which was mined prior to 1912. The regular smelters reported the recovery of 92 tons of antimony contained in antimonial lead scrap. The principal materials refined or remelted which contained antimony as an alloy were hard lead

drosses, babbitt, solder, pewter, and type metal. The 1913 imports of antimony as metal, in ore, or as oxide amounted to 7,692 tons, and the recovery from secondary sources was equal to 35.1 per cent of the imports. The secondary recoveries of antimony were 500 tons more than the antimony content of antimonial lead or antimony ores of domestic origin smelted in 1913.

Apparently there were no domestic tin ores smelted in the United States in 1913, though some tin concentrates were shipped from Nome, Alaska, Gaffney, S. C., and Spearfish, S. Dak., to Great Britain for treatment. This condition makes secondary tin an important factor in supplying domestic consumption. The secondary tin recovered in 1913 was equal to 27.2 per cent of the tin, as metal or as oxide, imported into the United States during the year (52,141 short tons). Secondary tin recoveries decreased from 15,401 tons, valued at \$14,301,368, in 1912, to 14,178 tons, valued at \$12,567,379, in 1913. The quantity recovered as tin was 6,415 tons and that in alloys and chemical compounds 7,763 tons. The value of the recovered tin here given is arbitrary and is based on the yearly average price given by the "American Metal Market." It will be noted that the secondary tin in alloys increased about 700 tons, an increase similar to that of lead in alloys. The secondary pig tin decreased about 1,900 tons, for although the reports showed that the recoveries from scruff and drosses compared favorably with former years, the recoveries from clean tin scrap, tin foil, and tin pipe were appreciably less in 1913 than in 1912. This condition was natural, for the use of tin foil and block tin pipe has not expanded and the recoveries from those sources are relatively small. The quantity of clean tin scrap treated was considerably less in 1913 than it was in 1912. This was partly due to the burning of the Vulcan Detinning Co.'s electrolytic plant at Sewaren, N. J., and to decreased operations of several other users of clean scrap tin. There was no great incentive to treat tin scrap which had been contracted for or purchased at prices that precluded much profit at the prevailing lower prices of pig tin in 1913.

The recovered tin includes the tin content of products made by several plants from tin scrap. These included some tin oxide, putty powder, etc., but consisted mainly of tin chloride. The production of these compounds is calculated as metal and not separately stated, in order to avoid disclosing confidential information. As the products are made from scrap tin and thus conserve the primary metal, they are properly regarded as recovered tin. Two forms of tin chloride are handled commercially—stannic and stannous salts. Stannic chloride is usually sold either as a water solution, called bichloride of tin, or as an anhydrous sirupy liquid, termed tetrachloride of tin, and is used principally in the silk industry. Stannous chloride is sold in the form of crystals and is used in dyeing and calico printing.

Most of the tin oxide, tetrachloride, and other products were made from clean tin-plate clippings or from tin liquors left in dyeing or weighing silks. The dry chlorine process was used to recover the tin from the clippings in some places. In others reverberatory furnaces were used to remove the tin coating, and a large quantity of tin was recovered in the form of a tin powder by the electrolytic treatment of clean scrap, the powder being sent to secondary smelters. The largest recoveries of tin were made from the scruff and drosses that occur in making tin and terne plate and amounted to over 5,000 tons. Only one firm reported using old tin containers, from which the tin and solder were first sweated and the black plate remelted to make sash weights. Comparatively large quantities of tin scrap and old tin cans are used in the western mining regions for the precipitation of copper from mine waters. Such scrap is plentiful, cheap, and fairly well adapted for the purpose. However, the tin coating of the scrap does not enter into the reaction and is lost entirely.

The principal alloys in which secondary tin was recovered were babbitt and other bearing metals, bronze, solder, pewter, and electrotpe metal.

ALUMINUM RECOVERY.

For the first time the Survey obtained statements of the quantity of secondary aluminum recovered as pig aluminum or in alloys, and while the inquiry may not have reached all producers, the result showed that the percentage of secondary aluminum used compared with virgin metal was fully as large as in other non-ferrous metals. The recoveries in 1913 amounted to 4,654 tons, valued at \$2,199,480. Of the 4,654 tons the quantity recovered in alloys amounted to 2,456 tons, and over 90 per cent of this was an alloy of 92 per cent aluminum and 8 per cent copper, used for making sand castings. It is probable that a large part of the secondary pig aluminum was recovered from clean clippings and borings and that it also was utilized in making castings.

PRODUCTION OF SECONDARY METALS IN THE UNITED STATES IN 1912 AND 1913.

Metal.	1912		1913	
	Short Tons.	Value.	Short Tons.	Value.
Secondary copper, including that in alloys other than brass.....	66,441	\$21,593,325	66,980	\$20,536,068
Remelted brass	101,523	27,279,516	99,315	24,651,969
Secondary lead	30,266	6,045,120	33,104	6,409,392
Recovered lead in alloys	36,902		39,730	
Secondary spelter	52,251	7,750,494	50,005	6,019,776
Recovered zinc in alloys other than brass	3,912		3,743	
Secondary tin	8,333	14,301,368	6,415	12,567,379
Recovered tin in alloys	7,068		7,763	
Secondary antimony ...	13	426,020	45	460,932
Recovered antimony in alloys	2,493		2,660	
Secondary aluminum ..			2,198	2,199,480
Recovered aluminum in alloys			2,456	
Total value		\$77,395,843		\$72,844,996

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NOTES AND COMMENTS.

Directory of Useful Minerals.

Every city has a directory of its inhabitants, giving the names of wage earners, and the addresses where each may be found. If you do not know a person's name but do know that he is a paper-hanger, the classified business directory will locate him for you. A directory of the useful minerals in the United States, on much the same plan, has just been published by the United States Geological Survey. If you want to know where any one of the 400 useful minerals occurs, this directory gives the list of localities in each state where your mineral will be found. If you do not know the name of the mineral but do know that it is an ore of silver or manganese, or carries asphalt or radium, the glossary will guide you to it.

The material in this bulletin is in two distinct parts. The first part consists of lists of the occurrences of minerals in each of the states, beginning with Alabama and ending with Wyoming. Under the name of each state the minerals found in that state are given in alphabetical sequence, and after each mineral name is given a list of the places where the mineral is found. The second part is a glossary of more than 425 names. Each definition is followed by a list of the states in which the mineral occurs. The glossary is therefore virtually an index to the first part.

Some mineral aggregates, such as clay, granite, limestone, sand, and sandstone, are included because

they constitute a very considerable part of the mineral production of the country.

This publication should be useful to many classes of people in many ways. If some one wants to sell you stock in a Texas oil company the report will tell you in what counties in Texas oil is produced and in what other counties it may eventually be found. If your wife wears a bloodstone lavalier, the report gives you the only locality in the United States where that stone is known to occur. If you want to manufacture plaster of paris or need lime for your back pasture, this report will tell you where to find the gypsum and gives the location of your nearest limekiln.

Herman Frasch.

Herman Frasch, president of the Union Sulphur Co., who died in Paris last May, was the inventor of the "Frasch Process" for mining sulphur, and is responsible for the development of the Louisiana mines, which have made the United States the largest sulphur producer in the world. Mr. Frasch was born in Gaildorf, in Wuertemberg, on Dec. 25, 1852. In 1868 he took up the practice of pharmacy, came to America, and was placed in charge of the laboratory of Professor Maisch, at the Philadelphia College of Pharmacy. His liking for industrial chemistry led him to establish a laboratory of his own in 1874. During the year 1876 he discovered a process for refining paraffin wax. His invention was purchased by the Cleveland Petroleum Company and he was induced to give up his work in Philadelphia and move to Cleveland to make the petroleum industry his specialty. He made a great success with his oil venture, and between 1876 and 1885 secured many patents for treating petroleum. In 1884 he was granted a patent for the manufacture of waxed paper, and prior to 1886 received several patents for an improved process for making carbonate of ammonia from salt. On Feb. 1, 1887, he applied for his first patent for refining Canadian and similar petroleum oils, and by Dec. 31, 1894, had received twenty patents for his inventions in connection with this subject. It was in the works of the Empire Oil Company that Mr. Frasch solved the problem of raising the offensive sulphur oils of Canada and Ohio from the low-grade fuel oils to the highest grade of pure oil. On Oct. 23, 1890, Mr. Frasch applied for his patent for an epoch-making improvement in the sulphur industry. With his new process Mr. Frasch was able to tap the rich sulphur deposits of Louisiana at a depth of 1,000 feet. He organized the Union Sulphur Company, erected plants and installed machinery. By his own process a single well delivered about 450 tons of sulphur a day. It is generally conceded that the deposits of sulphur and equipment of the Union Sulphur Company could close the Sicilian mines, but this was not the policy of the American concern. Plants were established abroad, but no attempt was made to cut prices or wrest trade from the Italian Consorzio.

Weathering of Coal.

The results of investigations into the weathering of the Pittsburgh coal bed at the Experimental Mine of the Bureau of Mines near Bruceton, Pennsylvania, are detailed in Bureau of Mines Technical Paper 35, which has just come from the Public Printer.

The authors, Horace C. Porter and A. C. Fieldner, outline the purpose and results of their investigation in the following manner:

The data obtained show the extent of alteration by weathering in the Pittsburgh coal bed as situated in this particular mine and will serve as a basis for approximate estimates of the alteration of the same bed in other mines similarly situated. The results have demonstrated that indications of weathering such as yellowish coatings of iron hydrate or a dull appearance of the surfaces, do not always signify a material change of the chemical composition or heating value of the coal itself.

The chemical analyses show that changes in composition have occurred in the coal for a distance of about fifty feet from the outcrop. The analytical data serve as a basis for certain deductions as to the nature of these changes. Several points of similarity become evident between weathered coal of this character and the Cretaceous coals and lignites. On the other hand, certain dissimilar properties of the two render it altogether doubtful whether a true metamorphosis or reversion of the bituminous coal to the lignitic type could ever take place through the agency of weathering. The analyses also show that the composition and heating value of the unweathered coal, computed on the moisture and ash-free basis, are fairly constant.

In addition to the usual analyses, special tests were made in order to show the relative oxygen-consuming power of the coal samples and their power of liberating inflammable gases, because these properties are known to vary with the nature of the coal and have a bearing on mining operations. As the direct union of freshly broken coal with oxygen lowers the oxygen content of mine air in places where ventilation is inadequate, and as the continuous escape of inflammable gas from broken coal tends to increase the danger of explosions, it is of interest to determine to what extent, if any, this behavior of coal is affected by proximity to the outcrop and consequent weathering.

Samples were taken at different points in the mine and put in 5-gal. glass bottles, the coal being crushed so as to pass a $\frac{1}{2}$ -inch screen; 20 lbs. were placed in each bottle as quickly as possible after the coal had been broken down and the bottle was sealed before it left the mine. By admitting air to the bottles in measured quantities daily and drawing off the air and gases the progress of oxidation of the coal and of the liberation of inflammable gas was followed. The samples thus tested were taken at 5 ft., 50 ft., and 620 ft. from the outcrop.

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SOME PROFESSIONAL OBLIGATIONS.*

By M. C. WHITAKER.

Chemical engineering as an organized profession is comparatively new, although many men have been engaged in this class of work since the beginning of large-scale manufacture. Since the organization of this institute, various definitions have been given to outline the scope of our professional activities, many schemes have been suggested to improve the training of our apprentices, some advances have been made towards standardization in our engineering practice, a code defining the ethical standards of our profession has been formulated and adopted, and we have shown our aims, with some results, in constructive patent reform.

Work of such a character is of the greatest importance, and is far in advance of that heretofore undertaken by any other organization in our field. It can never be regarded as completed, and the best thought and effort of well constituted committees will continue to be given to advancement along these lines, with great resultant benefit to the profession.

There comes a time, however, in the life history of every organization or enterprise when the greatest advancement and improvement may be made by a process of introspection. It would seem to the speaker that chemical engineers might now, with great profit to themselves and benefit to the profession, submit to a process of self-analysis. Obviously it would be out of time and place to attempt now a profound or philosophical analysis of our internal personal relations and aims, but it is hoped that by reference to a few of the more fundamental points we may thereby catalyze some productive reactions.

Chemical engineering must, sooner or later, come to be recognized as the leader among the engineering professions. Its interests are larger and more varied, and its scope is greater and more intimately related to social and industrial progress than that of any one or all of the other branches of applied science. Manufacturing output in the United States, which in money value is already almost equal to the largest single productive interest, will be dependent in some, if not in

all, of its steps upon the chemical engineer. The burden of the development of the industrial processes and the operation of the plants will fall upon him, and naturally the rewards of success and the odium of the failures will be his. The realization of the opportunities of such a profession, so full of brilliant promise and great possibilities, will depend in a large measure upon the breadth of view adopted in the acceptance of our responsibilities.

A voluble assertion of our importance will not give us the power to master our calling. Professional prestige, in the engineering field at least, is built upon achievement. Achievement worthy of the dignity of a profession cannot be built upon independent work, the spectacular results of a few individuals or the hit-and-miss strokes of fortune. It must be based upon a consistent development of and by a body of able progressive men, and be based upon years of unselfish constructive co-operation, in which each member contributes his share, and in turn, draws freely from the common store.

The legal, the medical and the clerical professions have devised for themselves some form of legal protection. The engineering profession, on the other hand, are subject to no form of external control, and may become self-developing or self-effacing according to the wisdom of the policies adopted in their direction and development, and the positiveness and value of their achievements. Merit, after all, is the only measure of success in engineering, and all failures, and even doubtful results, are promptly charged off against the profession.

The civil engineer may design and build a bridge. During construction his work is open and in full view of the public and his colleagues. There is not a single feature of his purpose, his design or his materials of construction which is not common knowledge to anyone who takes the trouble to look at his work, or read any of the numerous articles published during its progress. Even the lay public may be interested and pay their tribute to the man behind the work. The finished bridge stands in public as a monument to the power and ability of the builder and the profession he represents.

The mechanical engineer may design and build a wonderful machine. There is no secret about any of the features. His colleagues, the public, or anyone

*Presidential address delivered June 17, 1914, before the American Institute of Chemical Engineers.

may study and criticize his work, accept and profit by his suggestions and ingenious features, or may avoid his mistakes. The mechanical engineer has profited by the successes and failures of his predecessors in the art, and his successors, in their turn, will build better as a result of his work.

So it is with the mining and the electrical engineer. Each works with a full knowledge of what has gone before; each contributes his share to the advancement of his art, and the standing of the professions is enhanced because of his contributions.

The chemical engineer, on the other hand, works in unappreciated silence behind factory walls. He is not building a monument which invites public approval, though he may be making a product of equal value and more wonderful if it were understood. The details of his work are carefully guarded, and he is even denied the stimulus of public interest in his achievements. His designs, materials and methods often lack the helpful suggestions of his fellow engineers. He may repeat at great expense the mistakes previously made by his neighbor, or may fail to avail himself of well worked out methods which are unknown to him on account of lack of proper exchange of professional knowledge.

If he is secretive it comes as a result of environment and conditions. This secretiveness often becomes a habit and is assumed to be a necessity. At times this habit is extended either unconsciously or accidentally to ludicrous limits.

For example, note how difficult it is to find the professional or business connections of a chemist or chemical engineer. Surely there is nothing about this which should be concealed. On the contrary, good would result both to him and his employer by having his connections and field of activity well known. The directories of all other engineering societies contain valuable information about the professional activities of their membership, while our directories in many cases carefully disguise even the business addresses of our members.

The chemical engineer's efficiency in the production of successful results is reduced to a minimum, because of a lack of liberal professional co-operation, while civil, mechanical, electrical and other engineers are steadily improving their professional efficiency by a systematic exchange of principles and practices, and a selective action to carry forward the good methods and reject the bad ones. We of the chemical engineering profession are harboring conditions which retard or frequently even prevent professional progress.

When the work of the chemical engineer is not open to public view, his productive efforts not understood, and therefore not appreciated, his achievements cautiously guarded, his business connections withheld from the directories of his societies and absolutely no record of his professional activities is made available, is it any wonder the lay public usually think of him as a druggist?

If one traces the life history of the development of the chemical engineer, it will be found that we have some bad traditions to overcome. Our alchemist forefathers cultivated secretiveness, mystery, and even deception. These dark-art traditions are openly professed today in some of our factories, while in others they remain in latent evidence.

With these adverse conditions and traditions in existence it would seem that the chemical engineers are confronted with an important problem which intimately concerns the progress and development of the profession. Inefficiency and loss of prestige are bound to result from unsupported individual effort. Co-operation is essential to substantial engineering development. This co-operation comes about naturally in other engineering professions, and it will have to come, if not naturally then by force of necessity, in ours.

Every failure in design, every fatal accident, every industrial disease, every fire or explosion in a chemical works, every commercial insuccess is an indictment against the chemical engineering profession. Cause and effect in bridge failures, dam failures, boiler explosions, railroad and steamship wrecks are freely discussed in conventions and journals for the benefit of the interested profession. These open and frank discussions disarm public criticism on the one hand, and on the other place before all members of the profession most impressive and profitable lessons in what not to do.

The chemical engineer in such cases, apparently guided by his ancient traditions, or his environment controlled habits, as no other motive seems discernible, often secretes the facts not only from the public but also from his professional associates. Such secretiveness always arouses public suspicion. The interests of humanity may be sacrificed, and the profession, without the knowledge of what has happened, may go blundering into the same disaster again and again. These costly disasters are not even recorded as experience outside of the factory walls in which they occur.

Have the chemical engineers discussed or even heard of the causes leading to the failure of the coke plant at Bethlehem; the cause and effect of the explosion in artificial leather factory at Detroit; the lessons to be drawn from the recent fire in the Malinckrodt works in St. Louis; the cause and effect of the failure of a large gas holder at Philadelphia; the cause or remedy of the large number of industrial diseases in some of our plants; the complete failure of this or that piece of equipment or method of installation?

Do the affected or afflicted chemical engineers seek the assistance of their associates and professional colleagues in determining the cause, and suggesting the remedy for such disasters? If the cause and the remedy are determined, are the facts made public?

Think of the benefit which would come to our pro-

fession and to humanity and industry in general from frank authoritative discussion of these and many other problems which come within the experience of every chemical engineer. The discussion of the defective design, or material, or installation of chemical engineering appliances is a thing which would be of inestimable benefit, not only to other engineers, but also ultimately to the producers of the appliances. Negative results can be of no possible value to those industries which have developed them, but if they were published or discussed they would become of the greatest importance to future engineering progress. Why should they be jealously guarded and secreted and the progress of this profession thereby blocked?

The question as to what knowledge the manufacturer should disclose for public use and what should be kept within the factory walls is one which may be settled by the rule of reason, but never settled by yielding to the inclinations of our natural environment and our ancestral traditions. When it becomes clear that these conditions are blockading engineering progress and our own professional development, it will not be simply a duty, but an obligation, for every chemical engineer to apply this rule of reason.

Property value might safely be accepted as the basis for determining what should and what should not be disclosed. Manufacturers and chemical engineers would not be expected to give out unprotected information of direct property value any more than civil engineers would be expected to publish their working drawings before the contracts were awarded, or the mechanical engineer be expected to give away the appliances in which he had invested his time and his money. Such a policy would result in commercial anarchy and tend to destroy industrial stability and with it the dependent professions.

Fortunately it is very often the knowledge having the least property value which, when collected and classified, possesses the greatest professional value. Negative results can usually be disclosed without loss and they form the most substantial basis for engineering development.

On the other hand, the publication of the failure of a design, a material or a process would invite constructive thought from others which might turn a failure into a success, or suggest to our young investigators researches which would definitely establish or disprove the scientific validity of the principles involved.

The interests of humanity demand that industrial diseases, industrial accidents and improvements in working conditions be openly and frankly discussed in order that the combined effort of all minds be brought to bear on the needed solutions. Proper publicity in all bad or doubtful cases would do much to soften the hearts of the financial control, and at the same time independently enlist the services of the physiological chemists, the medical researchers, the

mill designers and many minds in our own profession which is most seriously indicated.

We have all heard the statement by members of this profession that there are no adequate textbooks or handbooks in chemical engineering of the same standard of excellence as those existing in mechanical engineering, for example. Such books, in any engineering field, are the results of compilations and classifications of approved matter from current technical journals and society proceedings, and it is inevitable that they will be large or small, dense or rare, profound or superficial, in direct proportion to the current available material.

If we secrete our information, or fail to publish our researches, hoard our knowledge and avoid the full and frank discussion of our industrial problems, we are bound to reap the negative rewards. Our books will not represent the sum of a profession's knowledge, but instead the comparatively small, laboriously attained work of one or a very few individuals.

This institute, representing as it does the leading organization devoted exclusively to developing the technical interests of the chemical engineers, and enhancing the prestige and value of that profession, should be the first to consider all obstacles to the accomplishment of its purpose. Our profession is built upon the applications of a science of the most infinite and varied detail. The mastery of modern chemistry requires a highly developed mind and one which should be fully qualified to attack and solve with ease the problems of policy in the development of the profession.

Our organization is new and the problems are large and numerous. Most careful consideration must be given to the direction of our energies into those channels in which we shall find the most productive returns. We have no time to waste on philosophical quibbling or fussy arguments. If self-analysis shows that the indictment of narrowness is valid and that the best interests of our profession will be served, as I think they will, by a more active interest in public questions, such as the so-called conservation movement, public service control, corporate regulation, financing of industrial enterprises, etc., then we should study and discuss these problems in our meetings and proceedings.

If chemical engineering education is twenty or thirty years behind the methods and efficiency of mechanical and electrical engineering training, as I think it is, and its improvement is being blocked by the dogmatic teaching that chemical manufacture is nothing more than enlarged laboratory practice, it then becomes evident that even more strenuous efforts will be required from this institute and its hard working committees to produce the desired results.

If, as I firmly believe, our professional progress is being seriously blocked by an unjustified and unjustifiable veil of secrecy or mystery drawn around our experiences, our needs, our achievements and our pro-

professional activities, the removal of this obstacle to our advancement becomes an obligation upon each constituent member of the chemical engineering profession, and particularly upon the Institute of Chemical Engineers.

THE INFLUENCE OF HEAT AND CHEMICALS ON THE STARCH GRAIN.*

By HENRY KRAEMER.

In presenting some of the most recent observations on the starch grain, it may be well to consider for a moment the nature and origin of starch. In a way starch is one of the most remarkable substances produced by the plant. It is the first visible product formed by the chloroplastid, or chlorophyll bodies, from the inorganic substances, carbon dioxide and water. Inasmuch as sunlight seems to be necessary to bring about this transformation the process is looked upon as one which involves the converting of the sun's energy into vital energy.

The substance thus formed by the chloroplastid through the influence of sunlight, in the leaves and other green parts of plants, is known as "assimilation starch," and serves subsequently not only as a food for the plant itself but is also the source of the energy of the animal world. Assimilation starch is not stored in the cells where it is manufactured, but each night through the influence of the plant ferments the starch formed during the day is converted into a soluble form, and transported to various other parts of the plant. In some cases this soluble starch is temporarily stored in the cells of the pith, medullary rays, or bark, and has received the name of "depot starch." While some of the soluble carbohydrate is converted into fixed oils and other substances, a considerable portion of it is carried to some reserve organ, as a root, tuber, rhizome, or seed, and under the influence of a plastid similar to the chloroplastid, converted into a stable form, known as *reserve starch*.

This is the product with which we are specially concerned in the present article. Heretofore, the minute study of the starch grain, particularly of its structure, has been of scientific interest only, but with the application of scientific methods in nearly every department of industry, it is coming to have a practical application.

The commercial reserve starches are derived from various plants, and not only enter largely into food products, but are also used for a variety of technical purposes. The grains of the reserve starches have a number of characteristic features. They vary in size, in shape, in internal structure, and also to a considerable extent in composition. The variation in composition is shown by the use of aniline stain and also by the use of iodine. By the treatment of starch with iodine solution, we may distinguish three kinds of reserve starch: (1) one which is colored deep blue, as

potato and maranta; (2) one which is colored somewhat purplish, changing to cinnamon-brown, as corn and wheat; and (3) one which is colored brownish-red, as in the amylo-dextrin starches of comfrey and a few other plants.

The shape of the grains varies from polygonal to ellipsoidal, the shape being influenced by the number of grains in a cell. Under the micro-polariscope the grains are seen to be anisotropic, the polarization effects differing with the grains of the different classes. Polarizing effects are usually produced by crystals, but may be produced by substances in a condition of tension, as minute globules of glass. It should also be stated that cell walls have this same property of double refraction, and it is very likely that the substances in the starch grains, as well as in the cell wall, are crystalloidal and arranged in spherite aggregates, resembling those of inulin, a product closely resembling starch.

The theories which have been advanced regarding the structure of the starch grain, have been largely based on studies of the potato starch grain. It was originally thought to be in the nature of a globule filled with a fluid. Fritche, Schleiden and others considered it to be made up of more or less concentric layers formed around a central or excentral point. While it may be true, as pointed out by Naegeli, that many of the reserve and glucose starch grains arise free in the cell, the view of Schimper that starch grains always develop within plastids, is generally accepted at the present time.

The internal structure of the starch grain is shown in several ways. When starch is treated with certain chemicals, or heated with water alone to a temperature of 60° C., the grains show a series of successive changes. First, the lamellæ or layers become more distinct, and the layers appear to be made up of parallel crystal-like particles, these latter being more numerous in successive alternate lamellæ. Then as the grain swells clefts which radiate from the center are formed. Later the center of the grain becomes hollow, and when the grain has swollen to about four times its original size the outer membrane breaks and the contents are gradually dissolved.

Some striking effects are also produced when starch is carefully treated with aniline dyes. The point of origin of growth and the successive layers alternating with it take up the stains, thus again showing the distinct character of the two kinds of lamellæ making upon the grains. When plant material containing mucilage is treated with aniline stains, the stain is taken up only by the cells containing mucilage, and this indicates that the lamellæ in a starch grain which take up the stains are composed chiefly of colloidal substances. From these observations it is apparent that the grains of certain of the starches, as the potato, if not of all the lamellated starch grains, are made up of two kinds of lamellæ, one rich in colloids and one rich in crystalloids. The presence of two kinds of

*From Original Communications, Eighth International Congress of Applied Chemistry. Vol. XVII, page 31.

lamellæ, at least in certain of the starch grains, and their difference of composition are further shown by the use of a weak solution of iodine, the so-called crystalloidal layers or lamellæ taking up the iodine and becoming blue.²

Recently I have been conducting some experiments to determine further the effects of heat upon the structure of the starch grain. When starch alone is heated to between 45° and 50° C. from 15 to 30 minutes, the lamellæ and the crystalloidal structure of the grains are brought out. The grain is so resistant that the inner structure does not appear to be lost until a temperature of over 125° C. is attained. Between 140° and 160° C. the polarization effects of the grains become faint, except in the case of potato starch, which now in addition gives chromatic effects. At 240° C. all of the grains are disintegrated except those of corn starch, the individual grains of which are of a brownish-yellow color and not perceptibly swollen. Besides the entire mass is more or less granular, while in the case of the other starches examined the charred mass is in a puffed condition.

The effects produced when starch is heated in the presence of a fixed oil, as almond oil, are of special interest. The inner structure of the starch grain is not usually apparent when it is mounted in a fixed oil, unless the starch has been previously heated to a temperature of from 80° to 160° C. When, however, a mixture of starch and oil is heated as high as 180 C. the grains still polarize light, which shows that the structure has not been altered. In other words the effects of heat on the grain are more or less neutralized by the presence of the oil. On heating the mixture up to 250° C. most of the grains still show their individual character, but no longer polarize light. They are but slightly swollen, and in the case of cassava and corn starch a central differential area occupies from one-half to nine-tenths of the original area of the grain.

It may be worth while to state that when starch and water in the proportion of 2gm. of the former to 100 c.c. of the latter, are heated together at a temperature of between 90° and 100° C. in a steam sterilizer seven or eight hours a day for a long period, even extending to months, dextrinization of the starch does not take place, that is, the solution still gives a blue color with iodine. Even though the operation be conducted in an autoclave under a pressure of 20 pounds for about ten hours, dextrinization is not effected. If, however, 1c.c. of N/HCl be added to 100 c.c. of water and this heated for five hours with 1 gm. of starch, the resulting solution is colored red with iodine. When the amount of the acid is reduced to 0.2 c.c. and the mixture heated under a pressure up to 12 pounds for one hour, cassava, corn, maranta and potato starch solutions give a deep blue color with iodine, while a solu-

tion of wheat starch gives a deep purple color with iodine. If the heat be continued an hour longer, wheat starch gives a purplish-red color, cassava a deep wine color, maranta and potato a light purple, while corn still gives a blue reaction with iodine.

These observations may be summarized as follows:

1. The starch grain consists of two nearly related substances: (a) a colloidal or mucilage-like substance which takes up aniline dyes, and (b) a crystalloidal or crystal-like material giving a blue color with iodine.
2. The starch grain is made up of concentric layers, one series of which contains a large proportion of crystalloids, while the alternate layers are composed mostly of colloids.
3. The polarization effects produced by starch are probably to be attributed to the crystalloidal character of the grains.
4. The starch grains retain their polarizing properties even when heated up to a temperature of 180° C., which seems very remarkable indeed.
5. At the higher temperature the potato starch grains give chromatic effects in addition, similar to those when a selenite plate is used.
6. While heating the starch grains in water rapidly changes the structure of the grain, it is only by the addition of chemicals or ferments that dextrinization is brought about.

THE GRADING OF MANILA HEMP.

The U. S. Consul-General, George E. Anderson, Hongkong, China, reports that the plans of the government of the Philippines for the official grading of Manila hemp and other fiber products of the islands have been established as law by the Philippine Legislature. The plan of classification and grading was adopted after most vigorous opposition on the part of Manila and other exporters of, and dealers in, hemp on the ground that the proposed grading and classification would do away with recognized brands of exporting firms, that it would be expensive, and that the colors, texture, strength, and other qualities of hemp were so various that it was impracticable to attempt to set up arbitrary standards for such purposes.

By the provisions of the new law, which will go into effect in January, 1915, the government proposes to establish fixed standards for the grading of Manila hemp or abaca (*Musa textilis*), the Manila maguey (*Agave cantala*), and sisal (*Agave sisalana*). These standards are to be determined by the Director of Agriculture, with the assistance of such experts as he may call to his aid, and shall be announced six months before the new act goes into effect. The new standard samples will be prepared in suitable form by the Bureau of Agriculture, and interested parties can secure such samples of the various fibers for use in grad-

² Kraemer, Bot. Gazette, Vol. XXXIV, Nov., 1902; Ibid., Vol. XL, Oct., 1905; reprinted in Amer. Jour. Pharm., Vol. 79, 1907, pp. 217-229; 412-418.

ing upon application and payment of the cost thereof.

The grading is to be done only in establishments licensed annually by the Director of Agriculture for the purpose. There are to be five classes of these grading establishments, graded according to the quantity of loose fiber they bale and grade, i. e., first-class establishments, handling 5,000 metric tons and more of such fiber; second-class establishments, handling between 2,500 and 5,000 metric tons of fiber; third-class establishments, handling between 2,000 and 2,500 tons; fourth-class establishments, handling between 1,000 and 2,000 tons; fifth-class establishments, handling between 500 and 1,000 tons; and sixth-class establishments, handling less than 500 tons annually. Fees are to be paid by these grading establishments of \$500, \$250, \$125, \$50, \$25, and \$12.50 per annum.

The fiber shall be graded according to the standards established by the government, represented by samples furnished for the purpose, but each grading establishment which is also an exporter of the fiber, may use private marks or brands in connection with the name of the official standard provided that such marks shall have been registered at and authorized by the Bureau of Agriculture. The fibers graded by these establishments shall be pressed into bales approximately of the following dimensions and weights: Length, one meter (3.28083 feet); width, 50 centimeters (1.6404 feet); height, 55 centimeters (1.804 feet); weight, 125 kilos, or 275 pounds net. The size of bale and other conditions applying to any particular grade of hemp in which excessive pressure would be injurious will be determined later by the bureau. The limit of the size of diameter and weight of each hank of fiber in the respective bales is to be announced at least six months before the law goes into effect. The hanks in each bale shall be of uniform color, size, and extraction, and each shall be tied by a portion of the same fiber. Every bale shall be free from strings, waste, tow, damaged fiber, fiber other than that which constitutes the bale or other extraneous matter, and the fiber shall be dry. No grading establishment can charge more than \$4 per metric ton for grading and baling any fiber covered by the act.

For the execution of the act the Director of Agriculture is authorized to open a special Fiber Inspection Office, with necessary sub-offices in hemp districts, and to appoint inspectors to be stationed at each export port and such other grading stations in the territory as may be necessary. The inspectors shall supervise the grading and baling of fiber and shall issue inspection certificates. A certain number of fiber inspectors are to be detailed to educate producers as to the manner in which they shall prepare their fiber to meet the requirements of the act. All fiber of which an official standard is established shall be graded and baled subject to the inspection of these officers. Every shipment of fiber shall be accompanied by a certificate of inspection, the certificate being transferred with the ownership of the lot covered by it.

TESTS FOR GALVANIZED PRODUCTS.*

The outward appearance of any galvanized article is not necessarily an indication of its excellence. This statement may be taken as a general rule applying to articles coated by either of the galvanizing processes mentioned herein.

For over 40 years prior to 1880 the hot galvanizing process, which was practically the only galvanizing process in commercial use prior to that time, was believed to produce uniform results. It was, therefore, not deemed necessary to test such coatings by any other means than that of durability under actual weather conditions. Observations made by Sir W. H. Preece, chief of the British Post Office Telegraphs, led him to see the necessity of a test for zinc coatings on telegraph wires.

Between 1880 and 1890 Preece devised what is known as the "copper sulphate test" for galvanized articles, and this test has until recently been accepted as the final word regarding the quality of any galvanized product. This test has been modified and standardized in the United States, notably by the chief engineer of the Western Union Telegraph Co., and has been quite generally adopted by producers and consumers of galvanized products, such as wire, sheets, line material, etc.

The original Preece test consisted in the immersion of the galvanized article in a saturated solution of copper sulphate for a period of one minute, removing, rinsing in water, wiping and again immersing in the copper sulphate solution. The number of immersions which the article could withstand before showing bright copper on the underlying steel or iron was taken as an indication of the excellence of the zinc coating.

As at present standardized careful preparation of the copper sulphate solution is necessary. The solution is brought to a density of 1.186 specific gravity at a temperature of 65° F. This solution is usually treated with a small portion of cupric oxide to neutralize any free acid which might exist in the copper sulphate crystals. Galvanized articles are first to be cleaned of dirt and grease by immersion in gasoline or benzine, then rinsed in water and wiped dry.

After this preparatory treatment the articles are given successive one-minute immersions in the standard copper sulphate liquor, held at a temperature of from 65 to 70° F., rinsed thoroughly in water and wiped dry after each immersion. The samples are to be carefully scrutinized after each immersion, and if spots of a clear copper color are observed the coating is said to have failed. The number of successive immersions which the article will withstand without showing indications of clear copper color is taken as an indication of the quality of the coating. A new portion of solution is to be taken for testing each article.

It will be noted that the Preece, or copper sulphate

*From a pamphlet, "The History and Development of the Galvanizing Industry," issued by the Meaker Co., Chicago, Ill.

test, determines only the thickness of the zinc coating at its thinnest portion. It is, therefore, not in any sense a determination of how much or how little zinc is deposited on the article under test. It is well known that the copper sulphate test is unsuitable for testing Sherardized articles, and it is a fact, however not generally known, that the copper sulphate does not attack zinc coatings deposited electrically, and by hot galvanizing methods at equal rates. It has been further demonstrated that the different temperatures of the molten bath and different methods of cooling articles galvanized in molten zinc show entirely unreliable results when subjected to the copper sulphate test. From these remarks it will be seen that it is unfair to test competitively zinc coatings applied by Sherardizing, hot galvanizing and electro-galvanizing methods.

Owing to the unsatisfactory results secured by means of the copper sulphate test, in a measure pointed out in the preceding paragraphs, an accurate quantitative test for galvanized products has been devised. The lead acetate test, as it is known, was recently originated by Prof. W. H. Walker, of the Massachusetts Institute of Technology, Boston.

The test is designed to show the weight of actual coating covering products galvanized by any of the well known methods. It takes into consideration the impurities residing in the coating and the main impurity usually found, i. e., iron, may be determined if desired. In practice, however, it is seldom carried out to this extent. The solution employed removes from the articles both the zinc and zinc-iron alloys present. The accurate weight before and after testing furnishes the basis for computing the quantitative value of the coating. It is unnecessary to take the time of sample immersion accurately, in which respect the lead acetate test differs from the copper sulphate test; however, the weighings, which must be accurate to one milligram, require considerable time and care. The lead acetate solution is prepared as follows:

Dissolve 3 lbs. of commercial lead acetate crystals ($\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + 3\text{H}_2\text{O}$) in one gallon of distilled water and add 1 oz. litharge (PbO). After complete solution of the lead acetate, the mixture should be stirred vigorously and any undissolved residue allowed to settle. The clear liquor is then poured off and the solution is ready for use. It is unnecessary to maintain any accurate temperature of solution as is required in the copper sulphate test, and the solution may be used for several tests without renewal, until such time as the action becomes too slow.

Samples of galvanized product are first to be thoroughly cleaned of oil and dirt by rinsing in benzine or in gasoline, then rinsing in cold water and dried with clean cotton waste. The sample should next be weighed to an accuracy of one milligram, and the weight noted. The sample is then ready for immersion in the lead acetate solution.

The length of time during which the sample is under treatment is usually about three minutes, although

it may be left in for a longer period without affecting the result. These immersions should be repeated until all of the coating has been removed and the sample exhibits the clean steel underneath. A short experience will enable the operator to tell with certainty when all of the coating has been removed. After each immersion in the lead acetate solution, the flocculent or loose coating of spongy lead which is deposited must be carefully removed; for this purpose it is usual to employ a small soft bristle brush, care being taken that no lead is "burnished" over the zinc coating. If any spots of lead are noted, which the solution does not remove, the careful use of a sharp knife is necessary. When the coating is all removed, the sample is then dried by immersion in alcohol and ignition, or by placing over a small steam coil. Final weight of the sample is then taken and noted.

If it is desired to estimate the amount of iron in the coating, the samples must be rinsed in clean water contained in a beaker, care being taken that all lead acetate and solution washings are saved. The lead acetate and the wash solutions may be put together and filtered, and slightly acidified with sulphuric acid; a few particles of granulated zinc should then be added, when the amount of iron is ascertained by titrating the solution with a standard solution of potassium-permanganate. The lead may be balled and squeezed with the fingers, and saved if desired.

The lead may be weighed and the amount of zinc coating removed may be calculated from the weight of the lead, the preferable manner of determining the amount of coating on the sample under test is as follows: Deduct the final weight of sample after treatment in the lead acetate solution from the original weight of the galvanized piece. Divide the net weight of coating so obtained by the weight of the bare or uncoated sample, whence the per cent of loss in weight is ascertained nearly enough for all practical purposes. Apply the per cent loss figure to 2,000 lbs. representing a ton of the articles in question. This will give the pounds of coating per ton of product.

Next, ascertain by close measurement or estimation how many square feet of surface there are in a ton of 2,000 lbs. of the articles under examination, reducing the pounds coating per ton, found by the application of the percentage figure, to ounces by multiplying by 16. Having the ounces of coating per ton and the number of square feet of surface per ton, divide the former figure by the latter, and find the ounces per square foot; this is usually a decimal figure. The ounces of coating per square foot gives a unit which may be used for the purpose of comparing the values of coating on different styles and kinds of galvanized product.

Samples of galvanized articles which are to be given the lead acetate test must, be, above all things, smoothly galvanized, without adhering lumps or drops of spelter, since these imperfections would lead to erroneous conclusions by adding to the net weight of coating particles of metal not evenly distributed,

wherefore the resultant ounces per square foot would be too high; it should be carefully observed that all portions of the galvanized article are coated, unless the uncoated areas are left out of the area figure per ton.

Professor Walker has rendered further service to those interested in testing galvanized materials by supplying a test which will show the presence or absence of pores or cracks in zinc coatings.

A strong solution of caustic soda in water is heated to a temperature of about 210° F., and the galvanized article suspended in this solution by a string or other non-metallic suspension. If pin holes or cracks exist in the coating, bubbles or hydrogen will be observed to come from the surface of the article at these points, while if there are no pores or cracks in the coating, no action will be observed. The caustic soda test will show whether or not the coating has cracked when the galvanized article is bent after galvanizing.

EXPLOITATION OF SPITZBERGEN COAL DEPOSITS.*

Coal dealers and merchants in Sweden expect to import considerable quantities of coal from Spitzbergen in 1914. A Swedish company has secured a large tract of land on the island, which is said to contain deposits of coal superior in quality to the best English product.

Not many years ago Spitzbergen was an unknown land, and for many years it was a resort only for whalers, fishermen, and bandits. Various scientific expeditions have returned from time to time with valuable and interesting information, but it seems never to have occurred to anyone that the island might become the seat of an important industry. It is only in recent years that a change has set in, and it is now apparent that in spite of ice, cold, and fog Spitzbergen is a land fraught with many commercial possibilities.

A geological survey of parts of the island shows that there are immense deposits of coal in various places, and interested individuals and companies alike are planning to tap these resources and bring them upon the highway of international trade.

It would appear that an American trading company first took a slice of territory at Advent Bay, where the coal deposits appeared on the surface. Then came the Norwegians, who were followed in turn by the Swedes, English and Russians.

A Swedish company was formed in 1911, with a capital of \$26,800, to exploit the coal deposits on the tract selected by its directors. This company may be said to form a continuation of the company founded in 1870 by the explorer Nordenskiöld, who was the first man to give thought to the importance of Spitzbergen's minerals. The Swedish company believes it has a tract richer than those pre-empted by other foreign companies. It is also believed that the operation of a coal mine equipped with necessary modern appliances would pay. Therefore everything has been prepared

for beginning operations in 1914. An engineer in the employ of the company has been stationed in Spitzbergen during the last two years, and he will continue in the same capacity after shipments begin.

There are many difficulties still to overcome, chief among which is securing a sufficient number of miners and properly sheltering them. For this purpose a number of small houses will be erected. It will also be necessary to construct a power plant.

The directors of this company believe that it will not take long to introduce these improvements and that coal shipments will begin in the summer of 1914, as planned. The coal is practically all on the surface, and deep mining will be unnecessary. If the freight problem can be solved, it is thought that Sweden will be able to supply considerable of its needs from this source. It will not be an easy matter, however, to compete with the English coal mines, which are so near at hand. The fact that vessels will be compelled to return to Spitzbergen without cargo also militates against the reduction of freight rates to the level of the average English quotations. The fact that the harbors of Spitzbergen are open to vessels to 1,000 of population was in the administrative county of West Suffolk, namely 39.33; and the lowest in the administrative county of Durham, 13.11. Of the county boroughs Great Yarmouth had the greatest number of old-age pensioners, 29.32 per 1,000, and Rotherham the lowest, 9.96. The figure for the city of London was 11.19 to the 1,000.

INDUSTRIAL GAS CALORIMETRY.

The investigations made during the past two or three years at the Bureau of Standards on the subject of gas calorimetry are described in a Technologic Paper of the Bureau under the title, "Industrial Gas Calorimetry." The paper has just been sent to press and will be available for distribution about June 1.

The investigation dealt mainly with the water flow type of calorimeter with a view to determining the sources of error to which such instruments are liable, the important precautions that should be observed and the accuracy attainable in their use. One calorimeter of the comparison type was included in the investigation.

Since it is now recognized that the heating value of a manufactured gas is its most important property the investigation is of importance in showing that the heating value of gases can be measured with an accuracy higher than is at present required for industrial use. The paper is of particular interest to those engaged in the testing of the heating value of gases.

The jute crop season of India just ended has furnished 9,600,000 bales, including the usual 500,000 bales estimated for Indian upcountry consumption. This is in excess of the final government forecast by about 1,000,000 bales.

*From Daily Consular Trade Reports.



METHODS OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR INSTITUTE OF TECHNOLOGY.

Methods of Analysis of Alloy Steels.

There are two general classes of alloy steels commonly found on the market, one which may be termed the alloy tool steels, and the other the alloy machinery steels. The constituents present differ somewhat both as to the ones present, and as to the quantity of each constituent which will probably be contained in the steel. It is thought best, therefore, to separate the methods of analysis into two divisions, giving in one the methods as applied to the alloy tool steels, and in the other the methods as applied to the machinery steels.

The constituents commonly present in the alloy tool steels are those found in the ordinary steel, such as silicon, sulphur, phosphorus, carbon and manganese. In addition to these there should be found tungsten and chromium, and sometimes nickel and molybdenum, although the last three, nickel, chromium and molybdenum are not commonly present. Methods are given in this article for the determination of the constituent commonly present in the alloy tool steels.

SILICON.

A two-gram sample is decomposed with 30 cc. of aqua regia, taken dry on the hot plate and baked for one hour at 110° C. The baked mass is taken up in hydrochloric acid and the insoluble matter filtered off, and washed free from iron with warm dilute hydrochloric (1:2). The tungstic and silicic acids remaining on the paper are washed twice with warm water and the tungstic acid dissolved from the paper with warm concentrated ammonia. The paper and residue are ignited in a platinum crucible and weighed. Ten cc. of hydrofluoric acid and two drops of sulphuric acid are added and the ignited material is evaporated dry on the hot plate, reignited and reweighed. The loss in weight is recorded as silica, and is calculated to silicon.

It may be objected that the treatment with ammonia dissolves some silica in addition to the tungstic acid, but the thorough baking and relatively small quantity of silica present in the samples worked with is believed to obviate this criticism.

TUNGSTEN.

One-half gram of the sample is decomposed on the hot plate with 20 cc. of aqua regia and evaporation continued until the material is just moist. Five cc. of nitric acid is added, evaporation on the hot plate con-

tinued to syrupy consistency and the beaker transferred to the water bath. The material is taken dry and dehydrated on the water bath for four to five hours. The mass is moistened with nitric acid and warmed on the water bath, enough water is added to dilute the nitric to about 1:3 and the residue is filtered off and washed free from iron with nitric acid (1:3). The filtrate and washings are set aside for use in determining chromium. The material on the filter paper is washed once or twice with hot water and the tungstic acid is then dissolved from the paper with warm ammonium hydroxide. The filtrate is caught in a tared platinum dish and evaporated almost to dryness on the sand bath. Nitric acid is added in slight excess and the evaporation continued to dryness. Subsequent ignition (preferably in a muffle) gives, by gain in weight, the tungstic oxide corresponding to the tungsten content of the steel. The per cent tungsten is calculated from this.

CHROMIUM.

The filtrate from the tungstic and silicic acids is evaporated nearly dry, 20 cc. of nitric acid and two grams of potassium chlorate are added and the solution boiled for ten minutes. Ten cc. of nitric acid and one gram of potassium chlorate are added and the solution boiled again for ten minutes. The chromium is now completely oxidized to chromate. The solution is diluted somewhat, allowed to cool, and neutralized with ammonium hydroxide. The solution is filtered from the iron hydroxide and washed with warm water. The iron hydroxide is redissolved into the original beaker with warm hydrochloric acid (1:1), reprecipitated and washed, the reprecipitation and washing being continued until the iron precipitate is free of chromium. (Three to four precipitations are necessary). The filtrate and washings are acidified with acetic acid and lead acetate is added in excess. The precipitate is allowed to settle, filtered off and washed a few times with water and dissolved into the original beaker with hydrochloric acid, (1:1). The solution is made up to about 400 cc., 20 cc. of a fifteen per cent potassium iodide solution are added and titration is carried out against tenth or twentieth normal sodium thiosulphate solution with starch as the indicator.

MANGANESE.

Manganese was determined by a slight modification of the Ford Williams method (B. S. circular No. 14).

Two grams of steel are decomposed with 30 cc. of aqua regia and taken very nearly dry on the hot plate. Nitric acid is added and evaporation repeated several times to replace the hydrochloric acid originally pres-

ent. Nitric acid (sp. gr. 1.2) is added and the insoluble matter filtered off and washed with nitric acid (1:3). The solution is evaporated to small bulk and 30 cc. of concentrated nitric acid and 2 grams of potassium chlorate are added and the solution boiled for ten minutes. Ten cc. of nitric acid to one gram of potassium chlorate are added and the boiling is continued for ten minutes. The precipitate is filtered on asbestos washed two or three times with strong nitric acid and then with water until free from acid. The asbestos pad is transferred to a flask, shaken up with excess standard ferrous sulphate solution until the manganese dioxide is dissolved, and the excess of ferrous sulphate is titrated with potassium permanganate. From this titration the per cent manganese is calculated.

NICKEL.

One gram of steel is dissolved in 25 cc. of hydrochloric acid (sp. gr. 1.16). The solution is filtered and the residue washed with hot water. One gram of tartaric acid is added to the filtrate which is heated to 50° C. Sufficient dimethylglyoxime solution containing 2.5 grams in 220 cc. of 98 per cent alcohol, is added to precipitate the nickel present. (1 per cent nickel requires 20 cc. of the glyoxime solution). The solution is made very faintly alkaline with ammonia, the nickel coming down as a scarlet, flocculent precipitate, which is filtered on a Gooch crucible, washed well with hot water, dried at 100° C. and weighed, the weight obtained being converted to nickel by use of the factor .2031. ($\text{NiC}_2\text{H}_{14}\text{N}_4\text{O}_{11} \times .2031 = \text{Ni}$).

SULPHUR: EVOLUTION METHOD.

Five grams of sample are dissolved in 60 cc. of hydrochloric acid in a 500 cc. Erlenmeyer flask fitted with a dropping funnel and connected to an absorption flask containing a strong solution of sodium hydroxide. The acid is run in quickly from the dropping funnel and the solution is boiled for fifteen minutes at the end of which time the steel must all be in solution. The contents of the absorption flask are transferred to a beaker, diluted to 400 cc. cooled and made acid with hydrochloric acid. Titration of the hydrogen sulphide present is made against twentieth normal iodine solution, and the per cent sulphur is calculated.

PHOSPHORUS.

Phosphorus is determined alkalimetrically modifying the usual method according to the suggestions of Cain and Tucker (B. S. Technologic Paper No. 24) to avoid errors due to the presence of vanadium and also to eliminate tungstic oxide.

Two grams of steel are dissolved in aqua regia and evaporated nearly dry, then taken up in 5 cc. of nitric acid and run nearly dry again to replace hydrochloric. Nitric acid (sp. gr. 1.135) and 10 cc. of potassium permanganate solutions (15 grams per l.) are added and the solution boiled. Sodium thiosulphate solution is added to dissolve manganese dioxide and the solution boiled and filtered. The filtrate is cooled to 15 to 20° C. and 5 cc. of saturated ferrous sulphate solu-

tion and 2 or 3 drops of concentrated sulphurous acid are added. The solution is heated to 80° C. and 40 cc. of ammonium molybdate solution are added and the solution shaken for 15 minutes at about 50° C. The precipitate filtered and washed with 1 per cent nitric acid, followed by 1 per cent potassium nitrate solution, until the washings are no longer acid. The precipitate is then dissolved in excess standard sodium hydroxide solution and the excess hydroxide titrated back with standard nitric acid, using phenolphthalein as indicator. The sodium hydroxide is standardized against prepared ammonium phosphomolybdate. The percentage phosphorus is calculated from this titration.

TOTAL CARBON: DIRECT COMBUSTION.

The electric combustion furnace is heated to above 950° C. and oxygen is run through the apparatus to displace the air. The oxygen passes through potassium hydroxide solution and over stick potassium hydroxide and then thru the furnace. The products of combustion pass through two U tubes containing respectively, granulated zinc and calcium chloride and then through a weighed Geisler absorption bulb. The liquid and solid potassium hydroxide free the oxygen from carbon dioxide and water. The granulated zinc removes acid and sulphur fumes from the gases of combustion which are dried by the calcium chloride and give up their carbon dioxide to the 50 per cent potassium hydroxide solution in the Geisler bulb.

Two grams of drillings are placed in an alundum boat which is pushed quickly to the center of the silica tube of the furnace (the latter being hot). Oxygen is passing at the start at a fairly rapid rate and is controlled so that bubbles are continually passing through the Geisler bulb during the run. The run is continued for 15 minutes. The increase in weight of the Geisler bulb, which has been previously weighed full of oxygen under atmospheric pressure, and which is again weighed under the same conditions, gives the weight of carbon dioxide corresponding to the carbon content of the sample.

The following analytical results were obtained on five commercial steels, using the methods described:

	A	B	C	D	E	F
	%	%	%	%	%	%
Silica	.18	.17	.28	.13	.18	.48
Manganese	.06	nil	.427	.065	.276	.290
Phosphorus	.01	.029	.038	.018	.052	.033
Tungsten	13.69	17.56	17.88	12.99	13.63	16.82
Chromium	2.35	2.33	2.54	3.90	2.48	1.50
Sulphur	.003	.009	.011	.025	.008	.015
Carbon	.56	.58	.52	.46	.70	.60
Nickel	nil	nil	nil	nil	nil	nil
Vanadium	nil	nil	nil	nil	nil	nil
Molybdenum ...	nil	nil	nil	nil	nil	nil

(To be continued.)

Improved machinery made in Germany has lately handled seed floss or silk cotton of the rubber vine, *Cryptostegia grandiflora*, so that a material resembling a light felt has been manufactured, which is adapted for life preservers and for suits of clothing to be attached to life preservers.

METHODS OF ANALYSIS FOR COPPER SALTS AND SOLUTIONS.*

By ALLAN J. FIELD.

The following article describes some simple methods of analysis that a plater who has had some chemical training can use, which would no doubt be useful to decide the superiority of one salt to another. Many of the copper carbonates on the market today are of varying composition and a chemical analysis would easily show the best and cheapest for the plater.

The composition of copper carbonate varies according to the method of manufacture; if it is not made correctly it will generally contain large quantities of basic sulphates, which are not desirable in a plating solution. The following two analyses of copper carbonates will indicate the great difference that exists between a carbonate that has been correctly manufactured and one that has not:

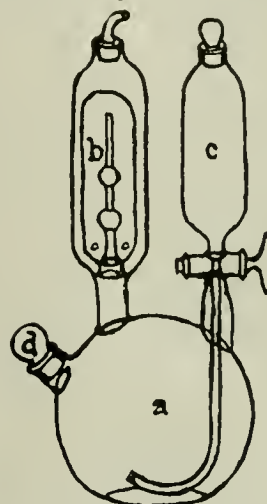
	Per Cent.	Per Cent.
Copper	53.00	48.25
Carbon dioxide	18.00	none
Sulphur trioxide	0.25	23.13
Iron	0.30	1.18

A true basic copper carbonate contains copper, 53.16 per cent; carbon dioxide, 18.39 per cent, the balance being oxygen and water of constitution and hydration. For copper determination the author has found the iodide method the most suitable, especially in laboratories not fully equipped for electrolytic analysis. The determination of copper in copper carbonate is as follows: Weigh off accurately 2.5 grams of the sample and transfer to a 250 cc. beaker. Add about 100 cc. of water and 25 cc. of concentrated sulphuric acid. When the carbonate is in solution place a piece of aluminum foil in beaker, which precipitates the copper cut in the metallic form. When all of the copper is precipitated, which can be shown by testing a small portion of the solution with hydrogen sulphide gas, a black precipitate indicates copper. Filter off the copper by means of a wad of glass wool placed in a funnel. Wash with hot water, then dissolve in concentrated nitric acid, receiving the solution in a 500 cc. Erlenmeyer flask. Boil the solution until all of the nitrous fumes are expelled. Ammonium hydrate is added to alkalinity, then boil again to drive off excess of ammonia. Add acetic acid in slight excess, heat gently until all of the copper is dissolved. Do not boil, as some of the copper might be lost by volatilizing. Cool the solution and transfer to a graduated 250 c.c. flask and dilute to mark. Take out 50 c.c. (.5 gram sample) into a 500 c.c. Erlenmeyer flask, add 10 grams of potassium iodide, shake and make sure all is in solution before commencing the titration. A standard solution of sodium thiosulphate is then run in to titrate the free iodine that has been liberated in the reaction. The end point is shown by means of a starch solution, which is added toward the end of the titration. A lilac color is produced when it is added. The

thiosulphate is added slowly until one or two drops turns the color to a cream, which is permanent without further change by the addition of more sodium thiosulphate.

Calculation: The number of c.c. of standard sodium thiosulphate used for titration is multiplied by the copper value for 1 c. c. and divided by 0.5 grams. Then multiply by 100, which will give the percentage of copper in the carbonate.

Standard Sodium Thiosulphate Solution: Dissolve 19.5233 grams of c.p. sodium thiosulphate in water and dilute to one liter. The solution should be kept in a brown bottle, as light has a tendency to decompose it. Standardize by dissolving one gram of pure copper foil in 25 c.c. dilute nitric acid. When all is dissolved transfer to a graduated 250 c.c. flask. Take out 50 c.c.



Schrötter Apparatus.

(0.2 grams of Cu.) with pipette into an Erlenmeyer flask and proceed as in the directions already given. The number of c.c. of sodium thiosulphate used for titration is divided into 0.2 grams, then the result will be the grams of copper in 1 c.c. of the solution.

Starch Solution: Take 0.25 grams of potato starch and a little water in mortar, grind together, then add to about 400 c.c. boiling water. Use about 1 c.c. for titrating. It does not last longer than a day or two.

CARBON DIOXIDE DETERMINATION.

This determination can be made quite quickly and easily by means of the Schrötter apparatus, which is shown in the illustration. To operate it, half fill the tube *b* with conc. sulphuric acid, and the tube *c* with dilute hydrochloric acid (1:1). Weigh off accurately about 2 grams of the carbonate and transfer to bulb *a* through the opening *d*. The entire apparatus is weighed carefully. Then run in slowly into *a* acid from tube *c* by opening stop cock. The acid should be run in slowly enough so that the carbon dioxide is not given off too rapidly to force the acid out from *b*. After all the reaction is over, the apparatus is gently warmed to drive off the carbon dioxide. Air is then sucked through the apparatus by opening the stop cock in *c*, then aspirating the air through tube *b*. When the apparatus has cooled to the ordinary temperature,

*From The Metal Industry.

it is again weighed. The difference between the weight before expelling the carbon dioxide and after is the amount of carbon dioxide present. Then if this difference is divided by the amount of copper carbonate taken, and the result multiplied by 100 will give the percentage of carbon dioxide in the copper carbonate. The determination of carbon dioxide by the Schrötter apparatus is not accurate within more than $\frac{1}{2}$ per cent. The principal error is due in weighing, the apparatus having such a large surface.

SULPHATE DETERMINATION IN COPPER CARBONATE.

As many carbonates contain basic sulphates, the amount present can be determined as follows: Weigh off 1 gram of the carbonate, transfer to a beaker, add sufficient dilute hydrochloric acid until all is in solution, then add about 200 c.c. water, heat to the boiling point and precipitate with a solution of barium chloride.

Let stand in a warm place until precipitate settles, then filter off, using a Schleicher & Schüll No. 590 filter paper, washing with hot water. Transfer precipitate and paper to a tarred crucible, the paper burnt off and the precipitate weighed as BaSO_4 , which multiplied by 0.343 = SO_3 .

The sulphate found is figured as SO_3 , as in some cases it can be in combination as sodium sulphate if the carbonate was not washed sufficiently, or as a basic copper sulphate.

COPPER DETERMINATION IN CRYSTALLIZED COPPER SULPHATE.

Dissolve 10 grams of the copper sulphate in water, transfer to a graduated 250 c.c. flask and dilute to the 250 c.c. mark with water. Take out 25 c.c. (1.00 gram sample) with pipette into a beaker, add about 100 c.c. water and 25 c.c. concentrated sulphuric acid, then proceed as in copper determination in carbonate. The % Cu found multiplied by 3.9283 = $\text{CuSO}_4 + 5\text{H}_2\text{O}$.

TO DETERMINE THE AMOUNT OF COPPER IN A PLATING SOLUTION.

The amount of solution to take for analysis depends upon the quantity of copper that is probably present. In an acid copper solution containing about 32 ounces of crystallized copper sulphate to 1 gallon of water; take 5 c.c. of the solution and proceed as in copper determination in carbonate. The calculation would then be: the number of c.c. of the sodium thiosulphate used times the copper value for 1 c.c. and divide by 5; then multiply by 524.5852 and the result will be ounces of copper sulphate ($\text{CuSO}_4 + 5\text{H}_2\text{O}$) per gallon. Example: 5 c.c. of the solution taken for analysis and required 61.1 c.c. of sodium thiosulphate solution and 1 c.c. of the solution = .005 grams copper; then $61.1 \times .005 = .3055 \div 5 = .0611 \times 524.5852 = 32.0$ ounces of copper sulphate per gallon.

The New Netherlands Petroleum & Asphalt Co. is to erect at Flushing, Holland, to handle 60,000 tons annually of Mexican crude petroleum.

NOTE ON THE DETECTION OF NICKEL IN FATS.*

By ROBERT H. KERR.

In testing samples of cottonseed oil, hydrogenated cottonseed oil, and mixtures of fats containing cottonseed oil, for nickel by the method of Boemer¹ a fugitive red color sometimes appears after the addition of the dimethylglyoxime and ammonia. This color closely resembles that obtained when a trace of nickel is present, but differs from that of nickel dimethylglyoxime, in that it is fugitive, appearing immediately after the addition of the ammonia, never before, and fading away almost entirely within a few minutes. Its appearance is apt to be very confusing, particularly to one not thoroughly familiar with it.

As there is no known inorganic body capable of giving such a reaction with dimethylglyoxime, it would appear probable that this reaction is due to some organic base contained in the oil and extracted from it by the hot hydrochloric acid. The fact that this reaction has been observed only with cottonseed oil, taken together with the well known fact that cottonseed contains numerous basic organic bodies, appears to corroborate this view. This hypothesis leads naturally to the conclusion that the trouble might best be prevented by the complete destruction of all organic matter contained in the acid extract.

Experiments have upheld this conclusion. A number of samples which had previously been found to show the fugitive red color to a marked degree have been found to show no trace of it after the destruction of all organic matter in the acid extract. As a result of this observation the following modification of the Boemer method is now proposed for the detection of nickel in fats.

Ten grams of the fat to be tested are heated on the steam bath with 10 cc. of hydrochloric acid (specific gravity 1.12), with frequent shaking for 2-3 hours. The fat is then removed by filtering through a wet filter paper, the filtrate being received in a white porcelain dish. The filtrate is evaporated to dryness on the steam bath, 2-3 cc. of concentrated nitric acid being added, after it has been partly evaporated, to insure the destruction of all organic matter. After the evaporation is complete the residue is dissolved in a few cubic centimeters of distilled water and a few drops of a one per cent solution of dimethylglyoxime in alcohol added. A few drops of dilute ammonia are then added. The presence of nickel is shown by the appearance of the red colored nickel dimethylglyoxime. The amount of nickel present may be estimated by comparing the color developed with that developed in a standard solution of a nickel salt.

A considerable number of samples, some of which had previously been found to give the fugitive color mentioned above, have been examined by this method

*From The Journal of Industrial and Engineering Chemistry.
¹Chem. Rev. Fett. u. Harz. Ind., Jahr. 19, Heft 9.

without any instance of the appearance of color not due to nickel. The residues from the evaporation are also purer and more readily soluble than when nitric acid is not used. A larger sample of the fat may be taken if desired. If this is done the amount of hydrochloric acid used for extraction as well as the amount of nitric acid added to the filtrate should be correspondingly increased. Samples as large as 200 grams have been handled with satisfactory results.

ADULTERATION OF COCONUT OIL.

For some months the impression has been gaining ground among the principal exporters of coconut oil in Ceylon that a considerable amount of adulteration is being practiced by native dealers, and that in some instances adulterated oil is sold in the local market to exporters who ship it in good faith to foreign buyers as the pure article. At the instance of some of the large exporters the attention of the Ceylon Agricultural Society and of the Department of Agriculture was directed to the question and an investigation begun.

According to the Daily Consular and Trade Reports the result shows that at the present time there is a very considerable adulteration of coconut oil by certain small native producers in the island, and that this oil has succeeded at times in getting into foreign exports. The principal adulterant used is peanut oil. This oil is imported into the island from India by chetties, a class of Indian merchants, and appears to be used for no other purpose in this colony than as an adulterant for coconut oil.

At present (Oct. 9) the price of peanut oil may be roughly taken to be slightly less than half the price of coconut oil. When cold pressed it is almost colorless, and, if mixed with coconut oil easily escapes detection unless carefully tested. Its specific gravity differs somewhat from coconut oil and the temperature at which it is inclined to solidify is considerably lower, so that an expert suspecting its presence would have little difficulty in detecting it. If the oil is obtained by the hot process, however, it is a dark yellow or sherry color and can be used effectively to adulterate only the cheapest grades of coconut oil. According to the customs statistics there were 56,324 gallons of peanut oil imported from January to June of 1913. During 1912 the imports were a little more for the full year, and it would thus appear that the adulteration of coconut oil is on the increase.

The eastern coast of India has always enjoyed a considerable trade in peanut oil. Originally it was shipped from Pondicherry, but since 1894 the trade has shifted to Madras ports, chiefly Cuddalore. In 1905-6 India exported, chiefly to France and other European countries, 2,472,334 gallons, for use principally in making lubricants and soaps, in the prepara-

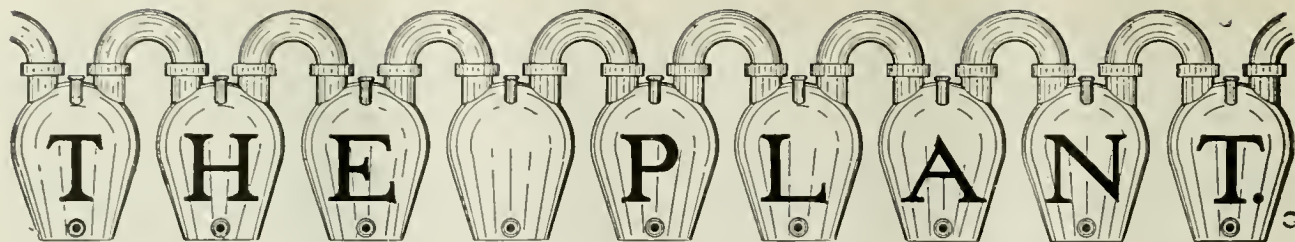
tion of edible fat, and as a substitute for olive oil. It is said that France annually imports from India and other sources about 250,000 tons of peanuts, and that Europe consumes about 150,000 tons of peanut oil each year.

The verification of their suspicion that adulterated cocoanut oil was being palmed off on them has alarmed cocoanut-oil exporters to such an extent that local buyers are refusing to purchase cocoanut oil from the small native dealers at any price, especially from the native dealers in the Galle district. It is said that between Galle, Matara, and Tangalle cocoanut oil is extracted by dealers in their own "chekku" mills, and that the adulteration is carried out by the middlemen who buy from these small millers and sell to the large dealers. As a result of the refusal of large firms to buy from the small oil millers within the last few weeks there exists a kind of deadlock in the oil trade at Galle, and even the reputable small native dealers hardly know what to do with their oil.

It may be said in all fairness for the good reputation of Ceylon cocoanut oil abroad that every effort is being made by the exporting houses to prevent adulterated oil from getting into their foreign shipments.

There is also another oil being imported into the island that is said to be used principally as an adulterant for lubricating oils, but also to a small extent as an adulterant of cocoanut oil. This oil is imported directly from a European country, but as it is known to be a petroleum product the suspicion is strong in local business circles that it originates in America. It is a bloomless and odorless white oil, and it can not be detected when used in the adulteration of vegetable lubricating oils. It was introduced into the market late in 1912, and so far has been imported almost exclusively by one native firm in the Pettah. During the first eight months of 1913 the total imports were 8,706 gallons, with a value, roughly, of \$5,300. It is said that the Government of Ceylon will investigate the adulteration of cocoanut and lubricating oils, unless the action of members of the chamber of commerce and other firms interested proves effective in putting a stop to it.

A new grain elevator will shortly be opened for public use in Constanza, Roumania. This will make the third elevator in that port which will be operated and owned by the government. The capacity of the Constanza elevators is 1,252,352 bushels each, divided among 250 silos of different sizes. The other elevators in the country are in Braila and Galatz, the two Roumanian ports on the Danube. The elevator in Braila contains 334 silos, which have a capacity of 1,071,418 bushels. The elevator in Galatz contains 334 silos, which have a capacity of 982,086 bushels. There are no other elevators in Roumania owned by the government nor by private parties, as the government owns all harbor lands.



WOOD DISTILLATION UNDER DIMINISHED PRESSURE—A CONTRIBUTION TO THE PROBLEM OF UTILIZATION OF WOOD WASTE.*

By MAXWELL ADAMS AND CHARLES HILTON.

The rapid decrease in the supply of long leaf pine available for the production of turpentine and the immense waste of resinous wood in the lumber industry throughout the country has stimulated chemists in an effort to devise some practical method for the extraction of wood turpentine from stumps, lapwood and mill waste. According to the Report of the Bureau of Chemistry¹ there are more than five million cords of waste wood left annually in the forests in the lumbering of resinous woods. The amount of waste is greatly increased when we add to this the dead and fallen timber of the uncut forest.

The methods for extracting turpentine from resinous wood, so far proposed, may be classed under four heads: 1. Destructive distillation, with or without steam. 2. Steam distillation. 3. Distillation with hot rosin. 4. Extraction with volatile solvents. These methods have all been tried out with varying degrees of success, but it is somewhat doubtful if any of them have developed beyond the experimental stage. The commercial success of any method will depend largely upon the demand for the by-products, and the utilization of all parts of the wood. The steam distillation process in conjunction with the manufacture of paper pulp appears promising² and the destructive distillation method has often been successful where charcoal, creosote and rosin oils are in demand.

The method described in this paper proposes to improve the ordinary destructive distillation process by controlling the temperature and diminishing the pressure at which the distillation takes place, thereby avoiding superheating and at the same time vaporizing the turpentine at a temperature below which it will not decompose.

According to Violette,³ when wood is carefully heated to 150° C. water only is distilled, and decomposition begins at about 160° C. These results will probably vary with the kind of wood. In order to determine the effect of heat upon the variety of wood to be

used in later experiments a sample of western yellow pine, *Pinus ponderosa*, was placed in a flask immersed in a sulphuric acid bath and heated very slowly. Care was taken that the temperature of the bath did not exceed that of the interior of the flask by more than five degrees. At 94° (the barometric pressure of the laboratory being 645 mm.) distillation of water and turpentine begins. When kept at 160° C. for several hours the wood turns brown, and above this temperature there is abundant evidence of decomposition. Gaseous decomposition begins when a temperature of 220° C. is reached.

Although pure turpentine distils at 155-6°, yet when dry wood is heated only a small percentage of the turpentine present is driven off when decomposition begins. This is explained by the fact that ordinary pitch as it occurs in wood is a solution of rosin and various waxes in turpentine; when a substance is dissolved in a liquid, the vapor pressure of the solvent is lowered at all temperatures, and the solution must therefore be heated to a higher temperature than would be required for the pure solvent, before distillation begins.

The rosin is not volatile; as the turpentine distils and the solution grows more concentrated, the vapor pressure is lowered, and the boiling point is correspondingly raised, until the temperature of decomposition is reached, and a large part of the turpentine is destroyed before it is vaporized. The presence of water in the wood, however, adds a factor which partly counterbalances this, and lowers the boiling point of the turpentine in the mixture. According to the law of Regnault⁴ for immiscible liquids, water and turpentine will distil at the temperature at which the sum of their vapor pressures is greater than atmospheric pressure, neither influencing the vapor pressure of the other. The quantity of each liquid found in the distillate will be proportional to their vapor densities and can be calculated by means of Avogadro's law.

A mixture of water and turpentine (the barometric pressure in the laboratory being 652 mm.) boils at 93° C. Water at this temperature has a vapor pressure of 588 mm. The remaining 64 mm. pressure must be due to the turpentine. The vapor pressure of pure turpentine⁵ shows that a mixture of it and water should boil at about 91° C. The slight solubility of each in the other doubtless lowers the vapor tension of both.

*From the Journal of Industrial and Engineering Chemistry.

¹ Bull. 159.

² Bur. of Chem., Bull. 159.

³ Sadtler's "Industrial Organic Chemistry," p. 348.

⁴ Pogg. Ann., 93, 537.

⁵ "Smithsonian Physical Tables," p. 126.

If we consider the gram molecular volume at 93°
 $\frac{22.4 (273 + 93)}{273}$
 as being ———— liters, and assume turpentine
 $\frac{136 \times 6}{652}$
 to consist of pinene with a molecular weight of 136,
 then the mixed vapors will be found to consist of
 $\frac{18 \times 588}{652} = 16.2$ parts of water vapor and
 $\frac{136 \times 6}{652} = 13.3$ parts of turpentine vapor. The ratio of the

will consist of $\frac{18 \times 31.5}{38.4} = 14.7$ parts of water vapor
 and $\frac{136 \times 6.9}{38.4} = 24.4$ parts of turpentine vapor.
 Thus the amount of turpentine vaporized is practically
 double that of the water, when the distillation takes
 place at 38 mm. pressure. These results are confirmed
 by experiment.

When we apply the steam distillation method to the
 extraction of turpentine from wood, the proportion of
 turpentine is very much diminished, and the distillation
 temperature is considerably higher, due to the presence
 of dissolved resins, which have greatly diminished the
 vapor pressure of the turpentine. Experiments show
 that, under the most favorable conditions, 15 parts of
 water remove 1 part of turpentine. The proportion
 of water, however, varies widely, depending upon the
 rate of distillation and the size of the wood chips.

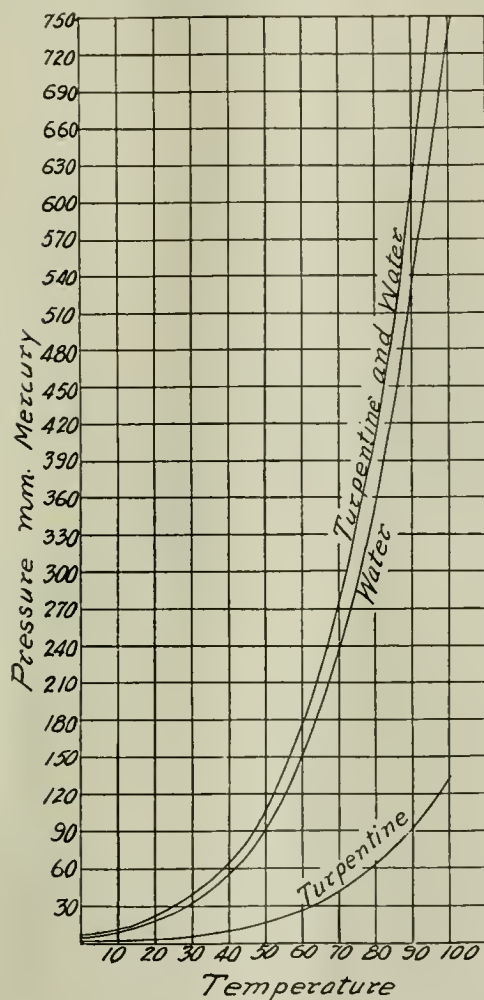


Fig. 1.

weight of water to turpentine in the vapor is approxi-
 mately 100 to 80, and this is also the ratio of their
 weights in the distillate.

The density of turpentine is 0.85, therefore the vol-
 ume of water and the volume of turpentine are prac-
 tically equal when the distillation takes place at at-
 mospheric pressure, but the proportion of turpentine
 in the distillate should be considerably increased when
 the distillation is carried on under diminished pres-
 sure, as is shown by the examination of the vapor
 pressure curves in Fig. 1.

The vapor pressure of turpentine at 30° is 6.9 mm.
 and that of water at the same temperature is 31.5 mm.;
 a total of 38.4 mm. By applying the preceding method
 of calculation we find that the mixed vapors at 30°

TABLE I.						
Number of fraction	Temp of oil bath $^{\circ}\text{C}.$	Temp. of dist. flask $^{\circ}\text{C}.$	Expt. No. 1 Press. normal		Expt. No. 2 Press. 35 mm	
			Vol. turp. Cc.	Vol. water Cc.	Vol. turp. Cc.	Vol. water Cc.
A	100-150	40-94	0.0	0.0	7.2	3.1
B	150-190	94-120	5.3	4.2	2.8	2.2
C	190-200	120-140	4.3	3.2	2.5	1.9
D	200-220	140-160	1.4	0.6	1.1	1.5
E	220-270	160-180	1.8	1.6	2.1	3.0
F	270-300	180-200	2.3	4.0	4.6	3.2
G	300-330	200-220	3.1	6.1	6.4	4.1

By decreasing the pressure, according to the pre-
 ceding theoretical considerations, the amount of the
 turpentine produced at a given temperature should be

TABLE II.							
		Expt. No. 3, press. normal			Expt. No. 4, press. 80 cm.		
		Vol. crude	Sp. gr. crude	Vol. refined	Vol. crude	Sp. gr. crude	Vol. refined
Frac.	Dist. temp. °C.	turp. Cc.	turp.	turp. Cc.	turp. Cc.	turp.	turp. Cc.
A.....	Up to 220	570	0.855	501	920	0.887	722
B.....	220-250	220	0.884	176	320	0.934	182

considerably increased. Accordingly, an ordinary dis-
 stilling apparatus, with a capacity of about 200 grams
 of wood shavings, was fitted up and attached to a

TABLE III.						
Variety of wood used.		Frac.	Temp. of distil. °C.	Time of distil.	Vol. of ref. turp. obt. at ord. press. Cc.	Vol. of refined turp. obt. at 80 cm. press. Cc.
Pinus	Monophylla	A	Up to 220	1 hr. 30 m.	180	250
Pinus	Monophylla	B	220-250	1 hr.	108	150
Pinus	Jefryii.	A	Up to 200	1 and ½ hr.	100	150
Pinus	Jefryii.	B	200-220	1 hr.	95	105
Pinus	Jefryii.	C	220-250	1 hr.	80	75

pump capable of maintaining the apparatus at a pres-
 sure of 35 mm. To avoid superheating, the distilling

flask was placed in an oil bath. A sample of thoroughly dry, western yellow pine, fairly rich in pitch, was cut into chips, which would pass through a half inch mesh. The sample was thoroughly mixed and 175 grams were used in each experiment, the results of which are given in Table I.

On account of the difficulties of heat control there was some variation in the oil bath temperatures of Experiments 1 and 2. The numbers in Column 2 represent the extremes of variation. Time being an important factor in determining the quantity of distillate obtained from wood, the temperature was raised

gaseous decomposition begins and diminished pressure can no longer be maintained.

In order to repeat the above experiments on a larger scale, a double-walled retort, capable of holding about 25 kilos of wood, and similar in form to the one described by Pritchard¹ was constructed.

The plan of the apparatus is shown in Fig. 2. Oil is passed through copper coils heated in a gas flame. The hot oil is forced to circulate through the outside jacket of the retort by means of a small centrifugal pump. By this means the temperature is under com-

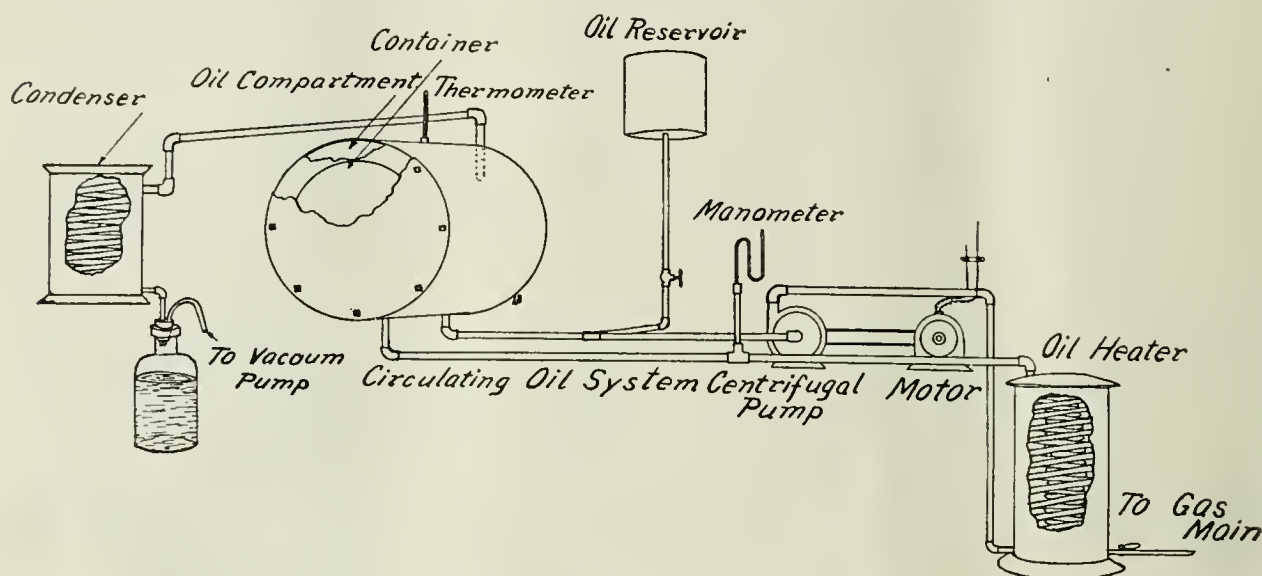


Fig. 2—Plan of Arrangement of Apparatus.

20° in approximately 30 minutes. Time and temperature thus being the same in both experiments, the variation in the amount of distillate secured in the different fractions must depend upon the pressure. The distillate coming over below 160°, the temperature at which the decomposition of wood begins is 20 per cent greater under diminished pressure than that distilling at ordinary pressure. The fractions coming over, both above and below 160°, under diminished pressure are much lighter in color than those distilling at atmospheric pressure. When the temperature reaches 220°

plete control and superheating is avoided. The door, through which the retort is filled, is closed with a ground joint, and made air-tight by means of set screws. The vapors from the retort pass through a condenser into a receiver, which is connected with a Geryk vacuum pump, capable of maintaining the entire apparatus, when in operation, at a pressure of 80 cm. The oil used to conduct the heat to the retort has a flash point of over 300° C. and is capable of withstanding a temperature of 400° C. without cracking, when heated in a closed vessel under pressure.

TABLE IV.

No. of fraction.	Temperature of retort °C.	Vol. in cc. of pyro. acid obtained.	Sp. gr. of pyro. acid.	Per cent wood alcohol in pyro. acid.	Per cent acetic acid in pyro. acid.	Vol. in cc. of tar obtained.	Sp. gr. of tar.	Per Cent Tar Distilling			Per cent pitch residue in flask.	Per cent water in tar.
								below 180° C.	between 180°-240°.	between 240°-320°.		
A	160-200	1275	1.002	0.49	0.64	835	0.855	83.5	3.0	2.1	9.6	1.8
B	200-240	560	1.013	0.91	1.13	280	0.884	62.5	4.2	5.0	27.2	2.1
C	240-270	885	1.041	1.43	4.01	590	0.930	39.6	12.8	14.6	31.1	1.9
D	270-280	675	1.053	1.65	5.06	420	0.953	25.2	16.9	19.2	35.8	2.9
E	280-290	1045	1.061	2.15	5.48	925	0.993	13.9	12.5	16.3	44.7	2.8
F	290-300	975	1.070	3.68	4.54	1000	1.025	10.1	12.2	14.3	61.4	2.0
G	300-360	920	1.073	2.67	2.65	960	1.032	7.4	11.2	13.8	65.3	2.3

To test the efficiency of the method, a sample of western yellow pine was cut into pieces one foot long and about one inch in diameter, thoroughly dried, divided into three equal portions of 22 kilos each, and subjected to the following treatment: I. Distilled in a retort by direct heat, without any attempt at temperature control or fractional separation of the crude distillate. II. Distilled in an oil-jacketed retort under atmospheric pressure. III. Distilled in an oil-jacketed retort under a pressure of 80 cm.

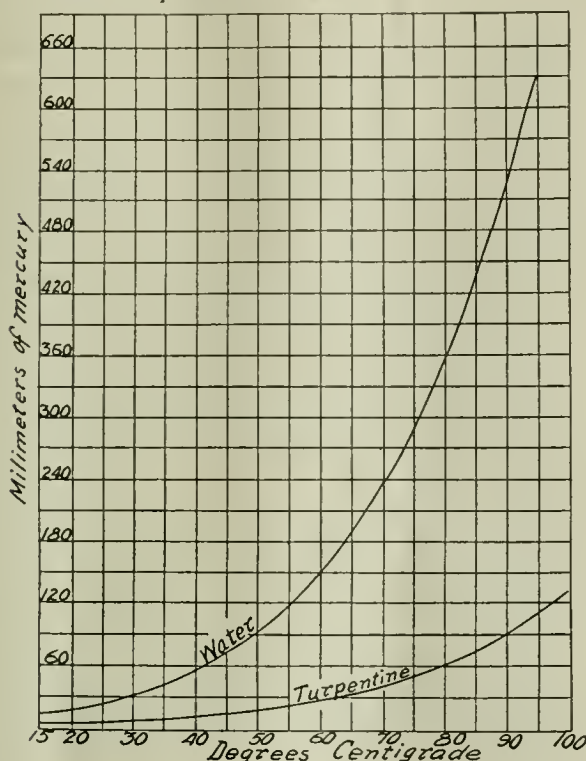


Fig. 3.

Method No. I yielded 1,606 cc. of tar from which was extracted 424 cc. of a light brown, ill smelling, wood turpentine, distilling below 170°. The results obtained from Experiments 3 and 4 are given in Table II.

Sample A is almost colorless and easily purified by distillation, but Sample B contains impurities, which can be removed only by alternately washing with caustic soda and sulphuric acid and redistilling.

Experiments 3 and 4 were repeated, using samples of other kinds of wood with results given in Table III.

From the above results it is evident that the yield of turpentine under diminished pressure is from 10 to 20 per cent higher than that obtained at ordinary pressure, using the same method of heat control, while it is double that obtained by the common destructive distillation method. In addition to this the quality of the product is much improved. If, however, as shown by a number of experiments in this laboratory, the wood used is green, and contains water in large excess of the volume of turpentine, then the process becomes one of steam distillation and the diminished pressure, while bringing the distillate over at a lower temperature, produces no decided increase in the total yield of turpentine.

The samples of purified wood turpentine, obtained from each of these varieties of wood, is water white and looks like ordinary spirits of turpentine, but they differ from it, and from each other, in odor and optical properties. They are under examination in this laboratory in an effort to identify the various terpenes present.

When the temperature of the retort reaches 250°, the volume of the gases given off is so great that the pump is no longer efficient in reducing the pressure, and distillation under diminished pressure becomes impossible. In order, however, to determine the total amount and the properties of the different products obtained at various temperatures from western yellow pine, 22 kilos of a sample of dry "light wood" were submitted to distillation in an oil-jacketed retort with results tabulated in Table IV.

After the distillation there remained 7.8 kilos of charcoal. The time for the distillation of each fraction was one and a half hours and the temperature was raised at almost uniform rate.

There are many varieties of wood indigenous to the Pacific coast, concerning the distillation products of which there is no published data. Samples of a number of these varieties, as they occur in the lumber districts of the Sierra Nevada Mountains, were submitted to destructive distillation. The results obtained

TABLE V.

Variety of wood used in the distillation.	Vol. of pyroligneous acid in liters.	Per cent wood alcohol in pyro. acid.	Per cent acetic acid in pyro. acid.	Vol. of tar in liters.	Per cent turpentine oil in tar.	Per cent creosote oil in tar.	Per cent mixed heavy oil in tar.	Per cent pitch in tar.	Per cent water in tar.	Kilos of charcoal.
Sugar pine	9.8	0.52	2.6	1.26	8.5	9.0	15.7	56.1	10.2	3.64
Yellow pine	12.4	0.55	2.2	2.09	10.6	6.2	20.2	46.9	6.5	4.32
Stump wood-pine.	10.9	0.57	2.4	3.50	18.1	9.0	20.4	50.4	2.4	4.09
Red fir	11.1	0.48	1.8	1.78	16.1	7.8	18.4	47.1	11.2	5.03
Silver fir	10.1	0.51	2.1	1.23	11.2	11.0	18.4	53.1	8.4	4.77
Mill states	9.6	0.61	2.7	1.81	9.2	8.1	20.7	48.8	11.8	4.53
Sage brush	9.4	3.54	11.53	1.94	...	16.2	14.7	15.6	48.0	7.8

are set down in Table V. The amount of wood used in each experiment was 25 kilos, and the methods used in the examination of the distillate are those described in Allen's "Commercial Organic Analysis."

The above experiments show that:

I. The western conifers contain wood turpentine in commercial quantities.

II. Under favorable conditions a cord (4,000 lbs.) of yellow pine will yield 25 gallons of wood turpentine.

III. The yield of turpentine from a given sample of dry wood can be increased by distilling under diminished pressure.

THE HEAT TREATMENT OF CARBON STEEL.*

By HUGH P. TIEMANN.†

In the present paper I have considered only pure carbon steel; that is, the alloys of iron with carbon. The principles involved are practically the same as when other elements are present, and certain exceptions are thus avoided which serve chiefly to render the subject more difficult of comprehension.

Heat treatment in its most general sense may be taken to mean the application of heat either to make the metal easier to work by rendering it softer or more ductile, or to secure certain desired (and beneficial) changes in its constitution and physical properties without mechanical work. By common usage, however, the term has become restricted to the latter application, for which the writer has suggested the following definition:

Heat treatment is the change or the series of changes, in temperature, and also the rate of change from one temperature to another, brought about to secure certain desired conditions or properties in a metal or alloy.

Heat treatment, like custom or common usage, goes back to the time "when the memory of man runneth not to the contrary," and we have no recorded history of its origin. Probably one of the earliest references to hardening by quenching occurs in the "Odyssey" in the passage where Ulysses, narrating the blinding of Polyphemus, the cyclops, with the heated stake, says: "And as when a smith dips an axe or adze in chill water with a great hissing—for hereby anon comes the strength of iron—even so did his eye hiss round the stake of olive."

The peculiar virtues of certain waters as quenching media *per se* was firmly held by the ancients, probably due to their unvarying coldness throughout the year, which insured uniform results. This is illustrated by a quotation from "Othello": "It is a sword of Spain, the ice-brook's temper."

Pliny mentions that oil was employed for quench-

ing small objects which would be rendered too brittle by similar treatment with water, thus proving that even in his time something was known of the relation between mass and quenching medium.

The present theory of heat treatment, which depends upon the constitution of the metal, is of very recent development. For example, in Agricola's "De Re Metallica" (first Latin edition of 1556) a description of the method of hardening employed by a smith states that after the pieces are shaped into a bar "while they are still glowing, he at once throws them into the very coldest nearby running water and in this manner, being suddenly condensed, they are changed into pure steel, which is much harder and whiter than iron."

The first definite theory advanced to explain the hardening and tempering of steel is probably that of Réaumur in his book "The Art of Converting Wrought Iron Into Steel" (1772). This is as follows: When steel is heated, certain salts are driven out of the metallic grains or molecules and form a cement between them which, by rapid cooling, is prevented from re-entering them. Reheating to moderate temperatures permits the absorption of a certain amount of the salt with consequent decrease in hardness. As a result of heating in a Torricellian vacuum he draws the conclusion which expresses the modern opinion: "The hardening of steel being due neither to the intervention of some new substance nor to the expulsion of air, the cause can be sought only in the changes which the structure undergoes."

Coming down to recent times the following are briefly the principal events in their chronological order, which are responsible for our present knowledge of the subject:

1864. Sorby (British Assoc.) published his work on the microscopic examination of iron and steel, which he had commenced the preceding year. This did not bear any fruit until after 1887, in which year he read, by request, a paper on the subject before the Iron and Steel Institute.

1869. Gore (Proc. Roy. Soc.) published the results of his experiments on the dilatation of steel at high temperatures. The method employed was a wire stretched horizontally which, by means of a series of levers, indicated the amount of expansion or contraction during heating or cooling. At a dark red, he found on cooling a greater dilatation than immediately above or below that temperature. He calls this phenomenon *recalcence*, because of the momentary brightening which accompanied it. He did not, however, observe the reverse effect during heating.

1873. Barrett (Phil. Mag.) carefully checked the work of Gore and found the reverse effect occurred during heating at nearly the same temperature as during cooling. He noted that this point was slight in the case of soft steels.

1880. Hogg stated that quenched steel showed less carbon by the Eggertz color method than the same

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steel annealed. About this time iron carbide, Fe_3C , was isolated from annealed steel by Weyl, Abel and Mueller.

1885. Osmond and Werth (Ann. d. Mines) published their paper on the cellular theory of steel.

In the years immediately following Osmond (Mem. Art. et Mar.) gave the results of his experiments on the transformation of iron and carbon, employing cooling curves obtained by means of a Le Chatelier electrothermic pyrometer.

1886. Pionchon made experiments on the specific heats at different temperatures, certain seeming anomalies pointing to allotropic transformations.

1890. H. Le Chatelier published variations in electrical resistance at different temperatures, confirming the results obtained by other methods.

1895. Osmond published (Bull. Soc. d'Enc.) his classical monograph on the "General Method for the Microscopical Examination of Carbon Steels."

1899. Roberts-Austen plotted the first iron-carbon diagram, corrected and amplified by Roozeboom, the following year, on the basis of the phase rule.

Other experimenters and scientists to whom particular tribute must be paid are Howe, Sauveur and Arnold.

The explanation of the various changes brought about by various heat treatments is based on the accepted theory that the element iron under proper conditions is capable of three, or at least two, allotropic modifications whereby certain of its properties differ considerably. To illustrate this it will be sufficient to cite the case of steel of a grade suitable for hardening. This can be effected by rapid cooling (usually quenching) only when heated above a certain definite temperature. At any lower temperature, no matter how rapid the cooling, it will remain soft. This is due to an allotropic modification existing above the given temperature which, by the rapid cooling, is preserved either partially or wholly in the cold state. If this were not so, the hardness should increase gradually when cooled from progressively higher temperatures, and not suddenly when a certain temperature has been passed.

In order to understand how heat treatment can produce such changes, the results of which in practically every case are shown by the properties of the material when cold, it is necessary to consider how steel is constituted or made up under different conditions of treatment or composition. We therefore have the physical constitution varying either with or without changes in the chemical composition.

Iron as an element is at present only a metallurgical curiosity, as its cost is very high. Also its practical application is relatively limited in comparison with that of its combinations which are capable of widely varying properties for all manner of purposes. Such a combination is commonly known as an alloy, even where the other constituents or ingredients are not metallic in character. The most important element to

combine with iron is carbon, the resultant substance (with carbon up to about 2 per cent) being termed steel. This element has a wider effect on iron than any other, and even when special elements such as chrome, nickel, vanadium, etc., are introduced its influence still predominates or governs those of the others.

It must not be supposed that the combination of iron and carbon is homogeneous throughout, that is, of uniform composition and texture, for this is far from being the case except under special conditions, for example, in the molten state or when at a high temperature. This condition is not due to segregation as ordinarily understood, but to certain phenomena which are peculiar to most alloys.

As the iron-carbon alloys present certain complications, it will be simpler to approach the subject by a study of what occurs when solutions containing different proportions of water and salt are cooled. If

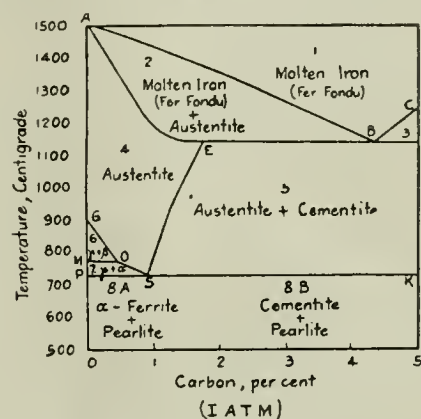


Fig. 1—Iron Carbon Diagram.

pure water is cooled, its temperature falls regularly until 0°C . is reached, when freezing occurs, the temperature remaining constant until all the water has frozen, after which the fall of temperature proceeds regularly. If a solution containing a small percentage of salt, say about 2 per cent, is cooled, freezing does not take place until a temperature below 0°C . has been reached, when, however, the entire solution does not freeze. Instead, small portions of nearly pure ice are gradually formed as the temperature is progressively reduced, the remaining solution, in consequence, becoming richer and richer in salt. This separation of ice is known as "selective freezing." Finally at -22°C . the temperature remains stationary until the remaining solution or "mother liquor," which now contains 23.6 per cent of salt, has completely solidified. This last freezing substance consists, not of crystals of salt dissolved in ice, but of separate, intimately mixed, microscopic plates of ice and salt. Such a mixture is termed a "eutectic" or "cryohydrate."

With a higher percentage of salt, say about 10 per cent, cooling proceeds to a somewhat lower temperature than in the preceding case before ice commences to separate out; but the final freezing point and the composition of the mother liquor are again -22°C .

and 23.6 per cent of salt, respectively, there being of course proportionately more mother liquor. If the solution contains exactly this percentage of salt, cooling proceeds without any separation of ice until -22° C. is reached, when the entire solution freezes out at this temperature. If more than 23.6 per cent of salt is in the original solution, then salt, instead of ice separates out initially, so that at -22° C. this composition is reached. It will thus be seen that no matter what the initial percentage of salt, the final composition at -22° C. is always the same.

Where retardations in the rate of cooling occur, due to freezing of part or all of the constituents, the respective temperatures are termed "critical" points or temperatures. If a retardation in the rate of cooling during a given range in temperature is observed, the designation "critical range" is employed.

A curve for a given composition, plotted to show the rate of cooling, is termed a "cooling curve"; a curve comprising the different critical points for a series of different compositions is known as a "freezing point curve."

As the important changes in the constitution of steel, and those which heat treatment is called upon to effect, occur after the metal has solidified it will not be necessary to consider here how it arrives in this condition, as the subject can be studied in treatise on metallography, where also the names and descriptions of the different constituents will be found.

It may at first be somewhat difficult to grasp the idea of changes occurring in solid material, but a little thought will show that the principal difference between a solid and a liquid is in the degree of mobility of the particles or molecules, as there is no sharp division. From water, as one extreme, whose particles are highly mobile, to a heavy oil, then, say, to molasses, then to highly heated steel which is readily forged and rolled, and finally to the same metal when cold (which can still be worked to a considerable extent, as in the case of wire drawing) as the other extreme, the steps are relatively gradual. We therefore properly speak of a "solid solution," in which the degree of viscosity is high, as similar to a liquid solution, such as the salt and water already discussed, in which the particles have great freedom of movement.

Fig. 1 is known as the "iron-carbon diagram," and is based on the work of various investigators beginning with Roberts-Austen and Roozeboom. It shows, according to the most recent information, the normal conditions which various iron-carbon alloys assume at different temperatures, as indicated by the different areas, the boundary lines showing critical temperatures in passing above or below which transformations (changes in condition) occur. These transformations are not instantaneous but require a certain amount of time for their completion owing to the lag or inertia (molecular viscosity) of the metal. Even with very slow changes of temperature on heating or cooling a

certain amount of lag is always present, being more marked when considerable amounts of carbon are present, and for this reason the position of the lines must be slightly lowered if cooling phenomena are being considered, and similarly raised (but to a less extent) for the reverse changes on heating.

The various conditions in which iron-carbon alloys may exist, depending upon the temperature and the percentage of carbon, constitute what are really different substances possessed of different properties and characteristics. To distinguish them names have been given, based largely on methods of nomenclature employed for mineralogical or chemical compounds. These names, with the definitions and descriptions most recently adopted by a committee of the International Association for Testing Materials, will be found in the proceedings for 1912, also reprinted in a number of technical books and periodicals. For the present purpose it will be sufficient to consider only that portion of the diagram comprising carbon up to about 1 per cent and for temperatures not exceeding, say, 1100 to 1,200° C.

The element iron has the peculiarity of possessing different properties which are normal in different ranges of temperature, a phenomena known as allotropy. Three allotropic varieties or modifications are generally recognized. (See Fig. 1).

Alpha iron, which is normal below M O S; *beta iron*, which is normal in the area G O M for steel with carbon up to about 0.35 per cent; and *gamma iron*, which is normal above P S.

Gamma iron can dissolve carbon (as a solid solution) up to about 1.7 per cent; is intermediate in hardness between beta and alpha iron; is non-magnetic. *Beta iron* (whose existence is still in dispute) can probably dissolve some carbon; is very hard; is weakly magnetic. *Alpha iron* can dissolve little if any carbon; is soft; and is strongly magnetic.

If pure iron (ferrite) is cooled from, say 1200° C., where it exists as gamma iron, the rate of cooling is regular until the point G on the line G O S is reached, when a retardation (Ar_3) occurs, due to the transformation from the gamma to the beta condition. The rate is then regular until the point M on the line M O is reached, when a second retardation (Ar_2) is observed from the transformation into alpha iron. With pure iron only there is no retardation at the line P S, the rate of cooling becoming regular after passing M.

If there is a small percentage of carbon, say 0.20 per cent, a somewhat different state of affairs is found at high temperatures. This carbon, either as such or in the form of carbide of iron (Fe_3C), is in solid solution in gamma iron, which is normal at this temperature, this solid solution being termed *austenite*. When the temperature passes the line G O (Ar_3), free iron in the beta condition is progressively expelled from the solid solution until the line M O (Ar_2) is reached. This beta iron is then transformed into the

alpha condition, the expulsion of free iron (also in the alpha condition) continuing until the line P S (Ar_1) is reached. At this point the austenite has been decreased in amount to such an extent that its carbon content has reached the eutectoid percentage (about 0.85 per cent), that is, what is contained in pearlite. After passing this line (temperature) this remaining austenite is transformed into pearlite, the gamma iron having been changed into alpha iron, whereby the carbon in solution is thrown out as carbide of iron (cementite). The final result is consequently pearlite and free ferrite.

With, say, 0.50 per cent carbon the same phenomena occur, except that there are only two transformation points, the two upper points previously found being now merged in one (Ar_{3-2}) when the line O S is reached. Also there is no formation of beta iron, the excess iron separating out in the alpha condition between the line O S and P S until, when P S (Ar_1) is reached, the remaining austenite has the eutectoid percentage of carbon as before.

With about 0.85 per cent to 0.90 per cent carbon there is only one transformation point at S (Ar_{3-2-1}), as in this case there is no need to separate any iron from the austenite to bring it to the eutectoid composition.

With higher carbons, when the line S E is reached, there is a separation of cementite (instead of iron) until at the line S K the austenite is again of eutectoid composition. Below this line the normal constitution of the metal is pearlite and free cementite.

It has already been mentioned that carbon is the element which governs or controls the physical properties more than any other. This effect appears to be due to: 1. Its condition; 2. Its distribution.

The condition of the carbon may be in solution in gamma iron, or else in combination with iron as the carbide, if the rest of the iron is in the alpha state. If the carbon is in solution it must be completely diffused or merged in the iron in the same way that salt is diffused when dissolved in water, forming one homogeneous substance in which individual particles cannot be detected even by the aid of the most powerful microscope.

If this solid solution of iron and carbon is preserved when cold by sufficiently rapid cooling, the complete diffusion must also be preserved.

By reheating to temperatures inferior to Ac_1 , the restraint of the atoms is sufficiently removed to permit the transformation of some or all of the gamma iron into alpha iron. The carbon originally in solution in this portion is thereby automatically expelled as cementite, resulting in the formation of pearlite. Unless the temperature is close to Ac_1 there is still too much viscosity to permit the molecules sufficient freedom of movement to cause any marked segregation

of the ferrite and cementite, so the pearlite has an extremely fine structure. Where temperature and time of cooling are sufficient the formation of relatively coarse pearlite will occur.

The segregation just referred to is not what is commonly understood by the term, and which is detected by ordinary methods of chemical analysis, but only in a microscopical sense.

In actual practice it is well known that of two similar pieces of the same steel, one merely annealed while the other is quenched and then reheated blow Ac_1 , the latter will possess considerably better physical properties, not only as regards strength, but ductility as well. The cause for this is clearly found in distribution of the carbon, that is, the material is microscopically more homogeneous.

Metals and alloys are composed of a number of crystals or grains. The irregularity of their form is due to the fact that the growth of each is interfered with by that of the others surrounding it. Therefore, it is only under special conditions that perfect crystals are attained. The size of these grains depends upon the maximum temperature above Ac_1 at which they have been free to develop, subject to the following conditions:

If a piece of steel is heated to a temperature corresponding to the point G in Fig. 2 (due to Howe), and is then cooled, it will be found to have a grain size O L proportional to this temperature. If it is then reheated the grain size will remain the same until Ac_1 has been reached. Immediately on passing this (as at N), the grain is refined to the minimum, that is, from N to J. If the temperature is still further raised the grain size increases progressively as shown by the curve J D G, and this cycle of changes can be repeated indefinitely, provided the steel is allowed to cool uninterruptedly from the maximum temperature above Ac_1 .

An experiment to show the effect of temperature on the grain size, known as "Metcalf's Experiment," illustrates this very clearly. A description of this experiment was published by William Metcalf in the Metallurgical Review (Vol. I, No. 3, November, 1877), and because of its value as well as the historical interest attaching to it, the following extensive extract is given:

To show this effect we take a bar of steel of ordinary size, say about inch by half, heat six or eight inches of one end to a low red heat, and nick the heated part all around the bar at intervals of half to three-quarters of an inch, until eight or nine notches are cut. This nicking is done at a red heat to determine the fracture at the nicks. Then place the end of the bar in a very hot fire, leaving the balance of the bar so much out of the fire as to heat it chiefly by conduction. Heat the end of the bar in the fire to white heat, or until it scintillates, and allow it to remain until the nick furthest from the end in the fire is not quite red, and the next barely

red. Now, if the pieces be numbered from one to eight, beginning at the outer end:

- No. 1 will be white or scintillating;
- No. 2 will be white;
- No. 3 will be high yellow;
- No. 4 will be yellow or orange;
- No. 5 will be high red;
- No. 6 will be red;
- No. 7 will be low red;
- No. 8 will be black.

As soon as heated as above described, let the bar be quenched in cold water, and kept in the water until quite cold. After cooling, the bar should be carefully wiped dry, especially in the notches. An examination of the different parts by the file will show the following, if high (carbon) steel has been used:

- No. 1 will scratch glass;
- Nos. 2, 3, 4 will be excessively hard;
- Nos. 5, 6 will be well hardened;
- No. 7 about hard enough for tap teeth;
- No. 8 not hardened.

In breaking off the pieces, which should be done over the corner of an anvil and the pieces caught in a clean keg or box to keep the fractures clean and bright, it will be found that:

- No. 1 will be as brittle as glass;
- No. 2 will be nearly as brittle;
- Nos. 3, 4, 5 will break off easily, each a little stronger than the other;
- Nos. 6, 7 will be very strong, and much stronger than No. 8, or the bar unhardened.

Place the pieces in the order of their numbers, fitting the fractures, then "up-end" each, beginning with No. 1 and following in the order in which they lie, and the result will be the series of fractures, each differing from the other.

No. 1 will be coarse, with a yellowish cast, and very lustrous;

No. 2 will be coarse and not quite as yellow as No. 1;

No. 3 will be finer than Nos. 1 and 2, and coarser than No. 8, and will have a fiery luster;

No. 4 will resemble No. 3 in color and luster, with somewhat finer grain, and will be coarser than No. 8;

No. 5 will be about the same size grain as No. 8, but will have fiery luster;

No. 6 will be much finer than No. 8, will have no fiery luster, will be hard through and very strong. This is what is called *refined* by hardening.

No. 7 will be refined and hard on the corners and edges, and rather coarser and not quite so hard in the middle. This is about the right heat for hardening taps, milling tools, etc., the teeth of which will be amply hard, while there will be no danger of cracking the tool.

No. 8 illustrates the original grain of the bar.

For the economical production of various shapes and sections by rolling or forging, it is essential to heat the metal to a relatively high temperature so it may be as soft and ductile as possible. If the metal were simply cooled from such a temperature it would be coarse-grained, and the cohesion between the grains would be weakened. This would mean increased brittleness and decreased resistance to shock, which would render the material unsuitable for many purposes.

However, when mechanical working occurs, the grains are reduced to a size dependent chiefly upon the temperature at which this work ceases and, in a

somewhat less degree, upon the size or mass of the piece, it being of course supposed that the work affected the entire section. The explanation for this is readily appreciated by referring to Fig. 3 (also due to Howe). The grains or crystals of iron in their normal condition being crystallographically to the isometric or cubic system, that is, their three axes are at right angles to each other and of equal length. When the length of a piece is increased by rolling or forging, there must be a proportional decrease in the cross-sectional area. The small grains or crystals which make up the structure must be deformed to at least the same degree. This produces a condition of unstable crystallographic equilibrium, since the axes are of unequal length. To regain the normal state each

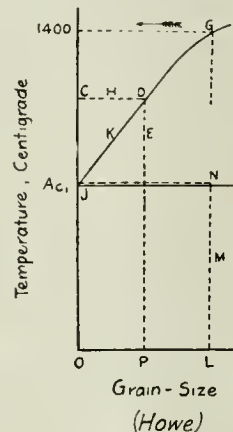


Fig. 2.

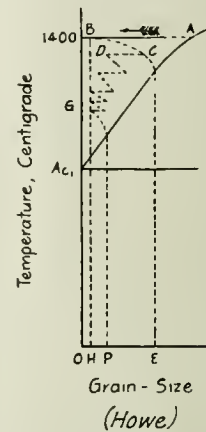


Fig. 3.

grain tends to split up into several grains of smaller size, depending upon the shortest axis which limits that of the other two. At the relatively high temperatures ordinarily employed for mechanical working, the molecules have sufficient freedom of movement to bring this about.

The curve Ac_1A is the grain-size curve of Fig. 2, just discussed. If a piece of steel at a temperature, and with corresponding normal grain size, as at A, is sufficiently deformed by a single operation of mechanical working, the grain size will be reduced from A to B, equal to O H. If the piece could then be cooled instantaneously, this size should be preserved. Under ordinary circumstances, however, the cooling requires some time. In this case the grain size, being below the normal for the existing temperature, increases progressively toward that normal size. Unless interrupted, the cooling of the piece and the increase in grain size from B is along the curve B C E. After crossing the curve Ac_1A no change in the grain size takes place, as already explained in connection with Fig. 2. The final size is consequently O E.

If, however, when C is reached, mechanical working is again applied, the grain is reduced to D. By further repetitions of cooling and working the zig-zag curve A B C D G is followed until G is reached. If this is the finishing temperature, the growth of the grain proceeds until, with the temperature steadily falling,

the curve Ac_1A is crossed, but this time at a much lower point than before, the final grain size being O P.

It will thus be seen that for pieces of the same size, that is, with the same rate of cooling, the grain size will depend upon the finishing temperature.

Theoretically, it would be desirable to finish just above Ac_1 , but, owing to the rapidly diminishing ductility, this is usually not practicable because of the danger of breaking or overtaxing the rolls or hammer, or of producing excessive strains in the material itself. This last is especially true if the piece is of very irregular section, since the molecules have lost much of their freedom of movement.

As a general proposition, the finest grain must be secured by reheating, because the piece can then be held a sufficient length of time at the proper temperature to enable the necessary rearrangement of the molecules to occur, which is not possible with mechanical working because the temperature is constantly falling.

Having taken up separately the various conditions which are met, we can now consider how heat treatment can be employed to obtain the best results. To this end we must secure as far as possible:

1. A fine grain size.
2. Fine and uniform distribution of the carbon and allied constituents.

Only in the case of eutectoid steel can this combination be met by simple treatment. What this is will be clear after considering a more complex (and usual) case. For the purpose of discussion let us select a piece of steel containing about 0.40 to 0.50 per cent of carbon. The steel as received will have been slowly cooled after rolling or forging. Its structure consequently will be made up of relatively coarse grains consisting of pearlite surrounded by or interspersed with envelopes or bands of ferrite, the latter being formed in cooling through the critical range between Ar_3 , Ar_2 and Ar_1 (O S and P S in Fig. 1). In order to obliterate this segregated ferrite it is necessary to obtain a homogeneous solid solution by reheating past Ac_3 ; subsequent cooling, if sufficiently rapid, will retain this solid solution when the piece is cold.

The temperature having considerably exceeded Ac_1 , the grain size is not at a minimum (Fig. 2). By reheating again past this lower critical point, however, the grain will be reduced. During this last reheating the excess ferrite has separated out, but at the temperature necessary, and provided the operation has been rapid, it has not had sufficient opportunity to segregate in any marked degree. The piece should then be rapidly cooled to prevent further segregation, and if harder than desired can subsequently be reheated to the proper temperature below Ac_1 .

These operations may be summarized as follows:

1. Heat (at any rate) just above Ac_3 and cool rapidly.
2. Heat rapidly just above Ac_1 and cool rapidly.
3. Heat rapidly to whatever temperature (below

Ac_1) is necessary, and cool rapidly or slowly, depending on the temperature.

In practice the combination of operations 1 and 2 are often referred to as "double quenching," and of 1, 2 and 3 as "triple quenching." Such refinements of treatment are, however, usually unnecessary for ordinary purposes, even when possible.

In the above discussion it has been assumed that the piece has been small, that is, without appreciable mass. The effect of mass will be taken up presently.

These are the fundamental principles of heat treatment, which are as true for commercial work as for laboratory experiments. In the former case, however, the effect of mass is an additional factor in the problem, presenting certain new features which must be carefully considered, as they are responsible for much trouble and misunderstanding. Following are the operations commonly employed in heat treatment:

Annealing. Reheating to a certain temperature, followed by slow cooling. To obtain the maximum benefits, including refinement of the grain, it is necessary to heat slightly above the upper critical point, Ac_3 ; this is sometimes referred to as "true annealing."

Hardening. Heating to a temperature above Ac_1 , usually above Ac_3 , followed by rapid cooling. This is usually secured by quenching in some liquid such as water or oil; if the section is sufficiently small, this effect may be obtained by air cooling.

Tempering or "drawing back." Reheating after hardening; similar to annealing, but usually to a lower temperature, in order to remove excessive brittleness, and affect the hardness as little as possible.

In practically all experiments which have furnished the information we at present possess, relatively very small pieces were employed. It is possible to heat or cool such pieces nearly uniformly throughout, about as rapidly as desired. When, however, the attempt is made to put into practice the principles so obtained, it is found that a new factor enters largely into the problem, namely, the mass of the object treated. For example, if a piece of fine wire is heated and then exposed to air at the ordinary temperature, it will be cooled almost instantaneously, while the time required in the case of a large shaft, even when plunged into cold water, will be many minutes.

Under similar conditions the rate of heating and cooling is much less for a large than for a small section, for two reasons:

First, because the distance to be traversed between the surface and the center, in the absorption or dissipation of heat, is greater. This rate progressively decreases as the temperature of the body, or of one portion of the body in relation to another portion, approaches that of the source of heat or refrigeration, in accordance with one of the fundamental laws of thermodynamics. Fig. 4 is intended to illustrate how the transference of heat occurs between different portions of the surface and the interior. A B C D is a section through an object uniformly heated or cooled on all

sides. The transference of heat to A B F E is through A B; to A E D through A D, etc. The progressive effect is indicated by the dotted lines which are rounded at the corners of the section, because in those regions it is obtained from two sides.

Second, because the cross-section increases directly as the square of the diameter, while the circumference increases only in simple proportion to the diameter. The same relation also exists between surface and volume (mass), since these are obtained by multiplying the circumference (or perimeter) and the area, respectively, by the same value representing the length.

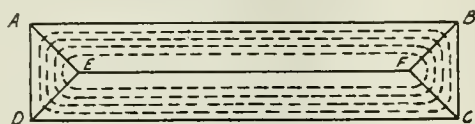


Fig. 4.

In Fig. 5 is a table of ratios between circumference and area for circles of diameters of 1 to 10. In the same figure are shown three circles with diameters of 1, 2 and 4. The hatched portions show graphically that the same linear distance on the circumference of each must serve for the transfer of amounts of heat which are respectively 1, 2 and 4; as already explained these ratios are the same if the surfaces and volumes (masses) are substituted. This may be summarized in the general law that for bodies of similar section the amount of heat transferred per unit of surface is di-

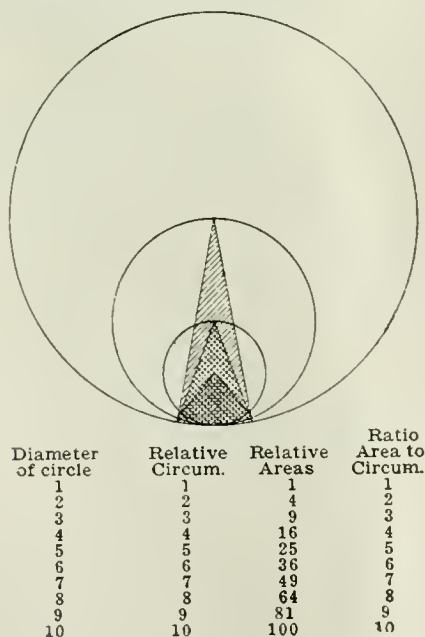


Fig. 5.

rectly proportional to the ratios of their diameters (or similar dimensions of their cross-section).

The preservation in the cold state of the condition which existed at the temperature to which an object is heated (above the critical point) is dependent upon a certain rate of cooling, irrespective of the size or mass of that object. With the means at our command it will readily be appreciated that a point is very quickly

reached when no method of cooling can compensate for the increase in mass, so that the rate of cooling decreases with corresponding increase in the actual time required.

As a direct result the interior of large masses will be cooled so slowly as to have only the properties of smaller masses cooled in the same time, or, in other words, the effect has been that of annealing rather than of quenching, as these terms are commonly understood. The exterior portion, although considerably retarded in its cooling by the necessary transfer through it of heat from the interior will be benefited in proportion to the rate at which its temperature was brought below the critical range, the properties of different portions of such a piece being in inverse proportion to the distance from the surface.

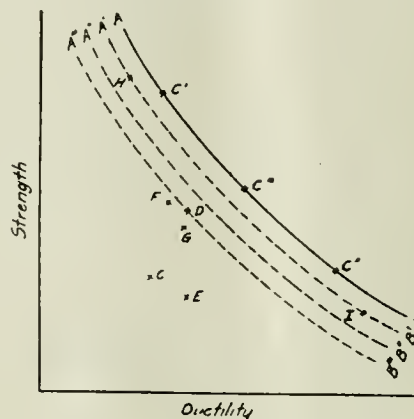


Fig. 6.

Fig. 6 is intended to show this state of affairs graphically, but without any claim as to its quantitative or even its qualitative accuracy. The curve A B is supposed to represent the maximum theoretical relation between strength and ductility for steel of any given composition; steels of other composition would be represented by curves varying progressively from one another. If it be tentatively admitted that this curve is correct, then a piece with the properties corresponding to the point A, with relatively high strength and low ductility, would be of equal merit with another piece with properties B, where relatively low strength is combined with high ductility; or with a piece with properties represented by any other point on the curve, since the curve is drawn on the assumption of a constant value for the relation between strength and ductility.

If a piece had only the properties C, the strength, according to our assumption, could be increased to C', the ductility remaining the same; or the ductility could be increased to C'', the strength remaining the same; or any other maximum relation could be attained, as C''', on the curve A B.

In actual practice or experiment, however, the factor of mass is bound to enter in, even with the smallest obtainable section, so that this maximum curve can only be approached but never quite reached. With

very small pieces the experimental maximum might be as represented by the curve A', B'; other curves A'', B'', A''', B''', etc., would, in the same manner, represent the possible maxima which could be attained by pieces of increasing section.

If the point C, for example represents the properties of a large untreated section, these could probably be improved by annealing to some point E, or by quenching and tempering to F or G. With cooling more rapid than usual, as by quenching in iced brine or liquid air, followed by tempering, the point D might be reached.

The reason for the higher relation of properties in a small section over that in a large section, treated under the same conditions, would appear to be due principally to the condition of the carbon. This is also borne out by the difference in the properties of test specimens cut respectively from near the surface and at the center of large sections, which has resulted in the clause in forging specifications that "the axis of the specimen shall be located at any point one-half the distance from the center to the surface and shall be parallel to the axis of the object tested," with a view to determining the average values.

Under suitable conditions of heating it is possible to secure a reasonably uniform temperature throughout a fairly large section. If the rate of cooling could then be controlled so that a large section could be cooled as rapidly (that is, in the same time) as a smaller object, the uniformity of the material in the two cases should be the same. As a matter of fact, however, such a state of affairs cannot be attained, as the conduction of heat from the center to the outside of a section of any size is relatively slow for the reason already given, and cannot be hastened sufficiently by any means at our command. Even if such were not the case, there is another insurmountable obstacle in the path. This is the possible introduction of excessive strains in large pieces, particularly where there is any irregularity of section. Rupture or incipient cracks resulting from this would not be corrected by any heat treatment alone.

We are therefore confronted with the contradictory state of affairs that the larger the section the more vigorous should be the cooling; and the more vigorous the cooling the greater the liability to excessive strains or rupture. While the component particles of the material may be advantageously affected, the object as a whole suffers. From this it is evident that for any given size or section there is a maximum relation between the ductility and strength, which decreases as the dimensions increase; that if the strength is maintained constant the ductility must decrease, and *vice versa*, as discussed in connection with Fig. 6.

CARDINAL POINTS AS TO RATE OF COOLING.

It must consequently be realized that the possibilities as regards the physical properties of large sections are not so great as in the case of small sections, and this must be taken into consideration in drawing

up the physical requirements of specifications. For, restating the case briefly, under similar circumstances:

1. The condition of the carbon and the grain size depend upon the temperature and the rate of cooling.
2. The rate of cooling depends upon the diameter or thickness of a given section, and probably also to a certain extent upon the length, or, in other words, upon the mass.
3. The rate of cooling through the critical range, and just below the lower critical point, is of much greater importance than during any subsequent tempering (after quenching).

To determine the uniformity of heating, the temperature must be of unquestioned accuracy. Further, the rate of heating must be carefully determined by experiment to secure proper penetration. It will be seen that the principles involved are comparatively simple. The main difficulty in carrying out the operations commercially is found in securing the necessary degree of uniformity. It is for this reason that special equipment is so essential. Of equal importance is the proper material, the composition of which must be definitely known, as variations, particularly in carbon, will result in different physical properties being secured under the same conditions of treatment.

CHEMISTS FOR GOVERNMENT SERVICE.

The United States Civil Service Commission, Washington, D. C., has announced an open competition examination on Aug. 3 for organic chemist, to fill vacancies in this position in the Bureau of Chemistry, Department of Agriculture, Washington, D. C., and a vacancy in the Hygienic Laboratory, Public Health Service, Washington, D. C., at salaries ranging from \$1,800 to \$2,500 a year. The duties of the position in the Bureau of Chemistry will consist of investigations in problems of organic chemistry relating to agriculture and the administration of the Food and Drugs Act in the Bureau of Chemistry. It is desired to secure persons having a thorough training in organic chemistry and in exact analytical chemistry. Physical chemistry, biological chemistry, particularly as applied to foods, drugs, bacteria, fungi, and agricultural plants are desirable qualifications. An examination also will be held on Aug. 3 for chemical engineer, to fill a vacancy in this position in the Bureau of Mines, Department of the Interior, for service at Pittsburgh, Pa., at a salary ranging from \$2,400 to \$4,000 a year. The duties of this position will be to conduct investigations in applied physical chemistry in its relation to fuels, oils, and gases.

The increased use of copra for oil production which has been witnessed in the last few years and which has led to the development of copra export and the planting of an immense acreage of coconut groves all over the Far East and in southern islands is leading to the establishment of oil factories.

PRACTICAL TEST OF EXPERIMENTAL PAPER.*

Howard F. Weiss, Director of the Forest Products Laboratory of the United States Department of Agriculture, has most courteously favored *Paper* with some notes on tests conducted by the Forest Service at St. Louis. As is well known to paper manufacturers, the United States Forest Service maintains laboratories at Madison and Wausau, Wis., for experimenting, among other things, on the utilization of pulp and paper. For the past two years there have been ground at the Wausau laboratory a number of woods to determine whether or not they would be suitable for the production of newsprint, and a preliminary account of this work was published in *Paper* for November 15, 1911. This work has been under the immediate direction of J. H. Thickers, engineer in charge of the laboratory.

From the large number of experimental pulps and papers which were thus made the director of the laboratory selected a few of the most promising for manufacture into pulp, which was later converted into paper at the mills of the Nekoosa-Edwards Paper Company, Port Edwards, Wis. The papers thus made were shipped to St. Louis, Mo., and through the courtesy of the St. Louis *Republic* run over the presses of that newspaper. Mr. Weiss assigned two of his staff, who are on duty at the Wausau branch laboratory, to oversee the experimental runs in the *Republic's* pressroom, and they were present both nights the paper was used, making close observations as the trials progressed. It should probably be added, perhaps, that the presses on which the paper was run were operated at a speed of 11,500 revolutions of the printing cylinders per hour, producing about 23,000 complete papers each hour.

Although the operation of the Wisconsin laboratory of the Forest Service has been repeatedly described in *Paper*, it may not be amiss to review here the laboratory's procedure and the results of the experiments recently concluded in the pressroom of the St. Louis *Republic*.

The laboratory was established about three years ago, for the purpose of securing substitutes for spruce in the mechanical pulp process. It was equipped with standard machines, a single unit of each kind. Arrangements were made whereby accurate determinations of power consumption, speed, pressure of grinding, etc., could be obtained.

A study was first made of the grinding of spruce, to find out definitely the effect on the quality and quantity of pulp produced by varying certain grinding conditions such as pressure, speed, surface of stone, temperature, etc. As a result of these experiments certain facts were noted, bearing upon the efficiency of grinding spruce, which are also applicable to the grinding of substitutes. As a result of the

tests on spruce, substitute woods can now be studied much more intelligently and thoroughly.

The study of substitute woods was then undertaken, the following species being tested:

Western hemlock	}	Pacific Coast
Sitka spruce		
Lodgepole pine		
Red fir		
Western yellow pine	}	Rocky Mountains
Western larch		
Lodgepole pine		
Hemlock	}	Lake States
Tamarack		
Balsam		
Jackpine		
White birch		
Poplar		

All these woods occur in large quantities in the sections from which they were secured, and in every case they are found in the vicinity of streams, capable of development for power purposes. Many of these woods, in fact all of those from the western part of the United States, occur in very large quantities in the National forests, and it is the hope of the Forest Service that they will be utilized in the future in the production of pulp and paper.

The experiments on these woods at the laboratory were conducted approximately in the following manner: A number of test runs were made until satisfactory operating conditions were found, the speed, pressure, and surface of stone being adjusted to secure the best results. A large quantity of ground woodpulp was then manufactured from each wood or combination of the woods under test and this was shipped to paper mills in the vicinity of Wausau. The ground woodpulp in each case were mixed with 25 per cent of hemlock quick-cooked sulphite, and were then run into newsprint paper under ordinary commercial manufacturing conditions.

As a result of the experimental work done on the different species, papers of the following fiber compositions were made at the mill at Port Edwards:

STOCK NO. 1.	
White spruce ground wood.....	75.0
Hemlock sulphite.....	25.0
STOCK NO. 2.	
Western hemlock ground wood.....	75.0
Hemlock sulphite.....	25.0
STOCK NO. 3.	
Sitka spruce ground wood.....	75.0
Hemlock sulphite.....	25.0
STOCK NO. 4.	
Montana lodgepole ground wood.....	75.0
Hemlock sulphite.....	25.0
STOCK NO. 5.	
Western yellow pine ground wood.....	75.0
Hemlock sulphite.....	25.0
STOCK NO. 6.	
Balsam fir ground wood.....	75.0
Hemlock sulphite.....	25.0
STOCK NO. 7.	
Cal. lodgepole pine ground wood.....	75.0
Hemlock sulphite.....	25.0
STOCK NO. 8.	
Red fir ground wood.....	75.0
Hemlock sulphite.....	25.0
STOCK NO. 9.	
Spruce ground wood.....	37.5
Hemlock ground wood.....	37.5
Hemlock sulphite.....	25.0
STOCK NO. 10.	
Balsam fir ground wood.....	37.5
White spruce ground wood.....	37.5
Hemlock sulphite.....	25.0

*From *Paper*.

STOCK NO. 11.	
Tamarack ground wood.....	75.0
Hemlock sulphite.....	25.0
STOCK NO. 12.	
Hemlock ground wood.....	37.5
White spruce ground wood.....	37.5
Hemlock sulphite.....	25.0

Rolls of these different papers were then sent to the *St. Louis Republic*, where they were printed under ordinary conditions on April 29 and 30, practically two entire city editions being gotten out. The tests at St. Louis were very interesting ones, particularly on account of being so satisfactory. The papers ran very well for the most part, and aside from poor color, there were no imperfections which could not be corrected.

The following is a statement by Mr. Knapp of the *St. Louis Republic* regarding the tests which were made. The color, while bad in many instances, will undoubtedly be greatly improved in the future:

The Wausau laboratory had as its main purpose the conducting of experiments to find woods that would serve as substitutes for spruce, and it was the product of this investigation that was given a practical test on the *Republic's* presses. The paper was used to print a part of the issue of the *Republic* on both Tuesday, April 29, and Wednesday, April 30, these trial runs being the first and only efforts so far made to use the experimental paper in a commercial way. The *Republic* volunteered to coöperate with the Government laboratory and is gratified that it can report the paper used was of a quality to justify hopeful anticipation that substitute woods can be used which will serve to hold a good part of the papermaking industry on American soil.

As already remarked, the experimental runs developed results that were quite distinctly encouraging. These, however, cannot be appraised with any measure of exactness for several reasons. First of these was the fact that there was not enough of any one particular make of paper to enable the pressmen in charge of the *Republic's* presses to acquire the familiarity that tends to good results. Sixteen rolls were sent for trial, and in only three instances were there as many as two rolls of the same particular composition. To make this handicap greater, it was necessary to constantly run two rolls of wholly different component materials at the same time, so that the press data were inevitably mixed and breaks in the running could not be traced with the same satisfactory certainty that would have followed if only one kind of paper at a time had been running on a press. The weight of the paper was, also, extremely variable, and the tension set for a roll running heavy would, of course, have to be set differently for another roll running much lighter in weight. Despite these handicaps, the demonstration was notably satisfactory in respect to running strength in more than one instance.

The conventional standard of the paper mills, in the matter of weight, is thirty-two pounds for 500

sheets measuring 24x36 in size, yet one roll of the experimental paper which weighed only 26.74 pounds had but one break. This particular paper was made from balsam fir and was of unmistakably good quality apart from its quite surprising strength. Another roll of the same composition ran without a single break and the trials apparently gave conclusive proof that balsam fir is good papermaking material. The red fir paper also showed good results, but the weight being 33.22 pounds, the demonstration was not quite so conclusive.

Taking all factors into consideration, strength, color, and finish, the paper made from balsam and spruce ground wood in equal proportions, roll No. 10, stock number, was the most completely satisfactory. This paper weighed only 29.24 pounds, and the five breaks that occurred in running it were attributed entirely to improper winding. The paper made from white spruce ground wood showed unexpected lack of strength, speaking relatively, but as might be assumed, was comparatively good in color. The matter of color is the point on which the most serious criticism can be made, but there is good reason for believing that this fault can be remedied. Consumers of paper always count on more or less difficulty at the start in getting the color established at a satisfactory standard, so this experimental paper cannot be fairly condemned on that ground.

But one kind of chemical pulp was used in the manufacture of these rolls, as the list already given indicates. It was hemlock sulphite in every instance. One roll, stock No. 2, was made entirely from hemlock, both ground wood and chemical pulp. This paper was somewhat dark, but it showed good strength. The press report shows five breaks, but they are attributed to winding rather than to the weakness of the paper, notwithstanding it averaged only 29.24 pounds. Paper manufacturers have used hemlock pulp for years, to more or less extent, but usually mixed with spruce, and it has never been ranked in the same class as spruce in the matter of quality. Ground wood made from hemlock has a tendency to develop unfelted fiber that stands up like whiskers on the surface of the paper, but the paper made from the Wausau laboratory pulp was notably free from this particular bad quality.

COAL PRODUCTION FOR 1913.

A production between 565,000,000 and 575,000,000 short tons of coal in the United States during 1913 is the official estimate of the United States Geological Survey, an increase over the record-breaking production of 1912 of 30,000,000 to 40,000,000 tons. These figures are given out by Edward W. Parker, coal statistician of the Survey, with the statement, however, that the coal-mining industry in 1913 lacked any spectacular features, the increase, in other words, being normal and an index of the general industrial activity of the country.

NEW DATA ON ELECTRIC SMELTING IN SWEDEN.*

During the last five years some very remarkable developments in the iron industry of Sweden have taken place by the introduction of electric reduction of iron ore, producing pig iron, and by electric refining of low-quality steel to high-grade steel. The system which has met with real commercial success is that of Electro-Metals, Ltd. Other methods have been tried repeatedly but they have all been abandoned and today the Electro-Metal furnaces are the only ones in use in Sweden. The following is a list of Swedish furnaces:

	Number	Power per furnace	Total power consumed
Working Now—			
Strömsnäs Jernwerks A. B....	1	3,000	3,000
Uddenholm A. B. Hagfors.....	3	3,400	10,200
Stora Kopparbergs Bergslag A. B.			
Domnarfvet	1	3,600	3,600
Building now—			
Strömsnäs Jernwerks A. B.....	1	3,000	3,000
Nykroppa Jernverk	2	3,400	6,800
	8		26,000 hp.

These furnaces will produce approximately 80,000 tons of pig iron per annum. The Stora Kopparbergs Co. are putting down 10 more furnaces, not included in the above. There are, further, a great many installations contemplated and it is certain that wherever there is cheap water power the old blast furnaces will be replaced by electric producers. Generally speaking, it holds good that wherever one horsepower per annum can be produced cheaper than the cost of two tons of charcoal or coke (depending on what class of iron is to be produced) it is a commercially successful undertaking to substitute electric heat for carbon heat.

The operation of the electric reduction furnace is much simpler than that of a blast furnace, and everybody who has been visiting the Swedish works returns impressed by the extreme simplicity of the affair. Fewer hands are required as well as less skill than for a blast furnace. The prime costs for the electric plant are also lower.

Tables I and II give all the data required for calculating the cost of one ton of iron produced. For a plant of three furnaces of 3,000 hp. capacity each. The following staff and labor would be required: One chief engineer, one assistant, two chemists, three foremen, two electricians, 10 men in each of three shifts.

At a meeting at Kristinehamn of the iron masters in the district last spring the following observations were made by the chief engineer of the Hagfors electric furnace plant after the first year's running:

The work with the foundations of our plant was commenced at the middle of April, 1911; eleven months later, or on March 15, 1912, furnace No. 1 was in operation, in August No. 2 was running, and now No. 3 is ready for starting up.

The plant was originally designed for two furnaces only, of 3,000 hp. capacity each (the power consumption is actually 3,400 hp.). The furnaces are placed in the central bay; on one side all the electrical gear is placed, transformers, switches, regulators, etc., this part being entirely isolated from the metallurgical part. The power is generated 9½ miles away at Forsshufvud, which power station belongs to the company. The voltage is 12,000 on the line and is reduced to low pressure by the transformers and adjusted by the regulators to between 50 and 100 volts as required.

The furnaces, as well as the whole of the plant, have been designed by the Electro-Metals Company and are mainly following the lines of the well-known Trollhattan furnaces, although the various details naturally show modifications based upon the experience from Trollhattan. There are six electrodes, cylindrical in shape and arranged to be used continuously without waste by screwing the ends together. The pouring bay is conveniently fitted with an electric

TABLE I.—CONTINUOUS RUN OF ONE FURNACE BELONGING TO STRÖMSNÄS JERNWERKS A. B. FROM OCT. 1, 1912, TO SEPT 1, 1913.

Number of charges	26,549
Weight of ore used, tons.....	11,338
Weight of limestone, tons.....	907
Weight of charcoal, tons.....	2,700
Produced pig iron, tons.....	7,258.3
Weight of charcoal used per ton of pig iron, lb..	830
Total number of hours when running normal, hr..	7,957
Total power consumed, kw.-hr.	15,291
Total power consumed per ton iron, kw.-hr.....	2,107
Weight of pig iron produced per 1 hp. yr., tons....	3.05
Weight of pig iron produced per 1 kw.-yr., tons....	4.14
Total consumption of electrodes, tons.....	28.42
Consumption of electrodes per ton of pig iron produced, lb.	8.7

overhead traveler as well as trolley tracks for transporting iron and slag. The iron can either be poured to pig or conveyed in ladles to the Bessemer and open-hearth works. The slag is run into block molds and makes excellent building stone.

The crushing room is at the end of the furnace building. There are three crushers of the ordinary jaw type. There is a railway track outside and the daily requirements are supplied in the trucks so that there is no need for big storing bins. One of the crushers is fairly large with wide enough jaw space for the biggest lumps, and the ore passes from the crusher to the smaller ones, and thence by a bucket elevator up to a belt conveyer above the charging platform so that the raw material may be unloaded where required. There is a small ore store, but this only contains some limited reserve amounts of the various kinds of ores used. These are from Taberg, Finnmossen and Nordmark. The charcoal is transported from the stores by a ropeway.

Up to now three different kinds of pig iron have been produced: For open-hearth treatment; for Lancashire treatment; for Bessemer treatment.

The quality which is desired for the open-hearth pig is semi-spiegel and contains Si, 0.40-0.60 per cent; Mn, 0.30-0.50 per cent; P, 0.011-0.018 per cent; S,

*From an article by Jens Orten-Boving in The Canadian Engineer.

0.015 per cent. It will be seen later on that it is more economical to produce pure spiegel iron in the electric furnace, and arrangements are being made to alter the open-hearth furnaces so as to use spiegel iron only. It has been assumed in various quarters that it would probably be difficult to maintain a constant product in an electric furnace. Experience shows, on the contrary, that a much more constant product is obtained from the electric furnace than from our old blast furnaces. One of the reasons for this fact is that there is such a large receiver or collecting basin in the lower part of the electric furnace that this collector acts as a regulator on the quality.

The Lancashire pig needed is quite white and has the following analysis: Si, 0.20-0.30 per cent; Mn 0.20-0.30 per cent; P, 0.011-0.018 per cent; S, 0.015-0.020 per cent. In the beginning there was a tendency for the sulphur to be unduly high, but this was put right by making the slag more basic whenever the furnace was run for Lancashire pig.

The analysis of the quality of Bessemer pig used is: Si, 1.00-1.40 per cent; Mn, 2.50-3.00 per cent; P, 0.015-0.019 per cent; S, 0.005 per cent. Excellent Bessemer has repeatedly been made of this pig. At first the result was not good, but it was soon found that we had to increase silicon and manganese. It had been assumed that the amount ought to be as usual, but the reason for the higher content being required is probably that the temperature of the electro-Bessemer pig is lower than for ordinary Bessemer pig from blast furnaces.

We intend, however, to rearrange the receiver in our electric furnace with a view to increasing the temperature. Our general experience points to the following results: It is cheaper to make spiegel than gray pig because: 1. More current can be put through the furnace. 2. The current consumption is lower. 3. Thus the production is higher. 4. The electrode consumption is lower. 5. The repair costs are lower.

It may further be stated that rich charges give bet-

ter results than poorer. The quality of the pig is not influenced by the percentage of iron contents of the ore. The electrode consumption has been relatively high and this is influenced by the following conditions: 1. High power consumption (which, of course, increases if the charges are poor). 2. Too lively gas circulation and too large a proportion of CO₂ in the gas. (Of course the carbon consumption is correspondingly lower). 3. Too large electrodes for the load. Since the 15th of January we have used the gas from the furnaces as fuel under our open-hearth furnaces and I estimate the value of the gas at from 2 to 3 shillings per ton of pig iron produced.

Finally, regarding the influence of the electric pig on the finished steel, our experience shows that the change tends to make better steel; this holds good both for Bessemer as well as soft and hard open-hearth steel.

The steel produced at Hagfors is of the highest quality and is mainly used for locomotive boiler tubes, piano wires and high-tension wires generally. Practically the whole of the output is exported.

In Sweden generally the electric reduction of iron ore is regarded as revolutionizing in this industry and elaborate preparations are being made for constructing mills of considerable capacity. Recent experiences have shown that larger electrodes can be used at the same time as the current intensity on the electrodes is increased. Larger furnaces will therefore be designed and some of those now projected will have a capacity of 8,000 hp. each.

It has been found that when using coke instead of charcoal it is advantageous to run on burnt lime, as otherwise the power consumption is too high, which largely depends on too much CO₂ being produced.

The Electro-Metals refining furnace is designed for 2-phase current, although 3-phase may be used by suitable design of the transformers and coupling the connections on Scott's system. The furnace has been correctly and carefully described in the July 25,

TABLE 11.—CONTINUOUS RUN OF THE TROLHATTAN FURNACE FOR THREE-MONTH PERIODS FROM OCT. 1, 1912, TO JUNE 30, 1913.

Period.	Oct. 1, 1912,	Jan. 1, 1913,	April 1, 1913,
	to Dec. 31, 1912.	to March 31, 1913.	to June 30, 1913.
Number of charges.....	6,193	7,107	7,281
Kiruna A ore	1,047	223.3	799.8
Tuollavara ore	973.4	123.3	762.6
Klacka-Lerberg ore	885.6	1,453	1,426.5
Persberg ore	8.82	47.97	148.4
Total ore	2,914.8	3,047.6	3,137.4
Limestone	169.94	252.8	273.5
Charcoal	699	719	738
Pig iron produced.....	1,905.86	1,933.32	2,000.14
Charcoal per ton pig iron.....	825	835	830
Actual working time.....	2,158.5	2,113.7	2,147
Consumed power, kw.-hr.....	3,957,565	4,095,588	4,216,544
Consumed power, per ton.....	2,076	2,118	2,108
Produced pig iron per kw.-year.....	4.22	1.14	4.15
Produced pig iron per hp.-year.....	3.10	3.04	3.05
Consumption of electrodes, total.....	5,307	8,670	7,896
Consumption of electrodes, per ton.....	6.2	10.0	8.8

Notes: The ore from Kiruna and Tuollavara is of the highest quality obtainable in Sweden. It will be seen that the output of the furnace as well as the consumption of electrodes depends largely on the quality of the ore used.

*From an article by Jens Orten-Booing in *The Canadian Engineer*.

(This furnace was run by the Swedish Association of Iron Masters with a view to establishing the practical success of the system as well as to give the various members an opportunity of trying their various kinds of ore. Thus, in the table different kinds of ore were used during the period indicated.)

1913, number of the *Electrical Review*. A number of these furnaces are now in operation in Sweden and in Sheffield, England, and the working results are highly satisfactory. To run this type of refining furnace is extremely simple, everything being so well arranged and balanced that any steel melter who knows open-hearth work can take charge of the electric furnace. No special training or skill is required from an electrical point of view.

These furnaces give a marvelous product inasmuch as it is quite easy to produce a high-class steel from any ordinary scrap with the greatest ease. The ordinary steel melter used to open-hearth work will not believe the results in the beginning, but once he has familiarized himself with the proper use of various slags to remove sulphur and phosphorus, as well as how to determine the carbon content or to add alloys, he will be loath to return to the open-hearth furnace which, indeed, is a very clumsy and incomplete apparatus compared with the electric refining furnace.

The process is equally suitable for high and low grade steel, for castings, drills, tool and quality steel of every kind and use.

The following figures, taken from an article published in the *Electrical Review* of July 25, give the actual costs of production.

WORKING COSTS PER TON STEEL.

	£.	s.	d.
Electrode consumption	0	4	0
Lining, roof, felting	0	6	0
Slag materials	0	2	6
Labor (assuming auto-regulation)	0	6	0
Tools	0	1	0
Electric energy, 825 kw.-hr. at 6d.	2	1	3
	3	0	9

These are actual figures taken from the works cost sheets and are obtained from a furnace of $2\frac{1}{2}$ tons capacity, so, naturally the figures are considerably reduced in larger furnaces.

It should also be noted that a very high rate is paid for the electric energy, as this is obtained from the municipal supply and is generated by steam. In utilizing water power, the current could easily be supplied at 0.2d per kw.-hr., corresponding to a charge of £6 per horsepower-year based on 300 days a year continuous full load; consequently, in using the above figures as a base to figure out cost of production in Canada it must be borne in mind that although the cost of labor would be undoubtedly higher, the cost of electric energy would be only one-third and the total cost, as shown by the above figures, would be in the neighborhood of £2 per ton.

If a new iron works were planned, electric reducing and refining should be used throughout and it is certain that with judicious arrangements adapted to the special requirements of the country such an undertaking would pay handsomely and the quantity obtained would be so high that it would exclude the importation of a good many standard products of iron and steel.

FINISHING TEMPERATURES IN ROLLING RAILS.*

The Bureau of Standards of the Department of Commerce has completed a report upon a series of observations of finishing temperatures and properties of steel rails by G. K. Burgess, J. J. Crowe, H. S. Rawdon, and R. G. Waltenberg of the Bureau staff. The main objects of this investigation were to determine from measurements taken in representative rail mills, the present American practice regarding the temperatures at which rails are rolled, to demonstrate the ease and accuracy with which such temperatures may be measured, to find out what the "shrinkage clause" in rail specifications really means, and finally to determine for rail steels some of the physical properties, particularly those of interest in manufacture, some of which, it would seem, are not sufficiently well known as yet. Among these last are the expansion, melting ranges, critical ranges and temperature distribution throughout a rail section on cooling. The main points in the report follow:

It is generally recognized that the factor of greatest importance in the manufacture of rails is the making of sound ingots. But it is also acknowledged that, starting with sound ingots in the rolling mill, the quality of the rails produced will depend in a very considerable measure on the process of rolling, and in particular on the temperatures. The undesirable effects of rolling too cold and too hot were very early recognized, but there is not complete agreement or conclusive evidence regarding the effects of finishing rails too hot.

The usual argument, briefly stated, is as follows: Rolling steel below the critical range distorts and weakens the crystalline structure, while rolling and finishing at temperatures too high above the critical range produces a coarsely grained steel which is weaker than the finer grained structure obtained by doing work continuously on the rail down to the critical range, which usually lies between 650 and 750° C. (or 1200 to 1400° F.) for rail steels, and is rarely above 700° C. (1300° F.).

The manufacturer prefers to roll his rails hot, as less power is then required to operate the mill and there is less wear and tear of the rolls so that, in practice, fixing a lower temperature limit is of relatively less importance, although the results of too cold or uneven rolling should not be overlooked in framing specifications.

It appears to be the general opinion that with the high carbon rails of heavy section, with their greater tendency to brittleness, now so generally manufactured, the necessity of more closely limiting the upper temperature of rolling is of greater importance than with the lower carbon rails of a few years ago. Nevertheless, an examination of the specifications generally in use for the purchase of rails in this country, will show

*From the *Iron Age*.

that there has been a tendency to raise rather than lower the allowable upper limit of finishing temperatures as defined by rail shrinkage, and the question arises whether this specification should not now be subject to revision, both as to its numerical value and as to the manner of its measurement. More experimental work will also have to be done before satisfactory specifications can be drawn as to finishing temperatures, and it would be highly desirable if one or more of the mills could make a series of a considerable number of rails (several thousand at least) as similar in all other respects as possible but each series rolled at a definite well determined temperature. This would not be difficult of accomplishment and a record of their behavior in the track could easily be kept.

In pursuance of this investigation a series of measurements of ingot and finishing temperatures were made at four representative rail mills, designated by A B C and D. The portable pyrometer used was the Holborn-Kurlbaum type of the Morse instrument. Temperature observations were taken by sighting on the rail bars at the instant of cutting by the hot saws, the pyrometer being located so as to view the head of the rails at the first saw, except for mill C, at which, for convenience, the base of the rails was sighted as they passed to No. 1 bed. Since mill C was rolling a rail of heavy base, the measurements are comparable with those made by sighting on the heads. This was also controlled by direct observation.

The only considerable element of non-uniformity of the measurements at the several mills lies in the fact that the distance and time from the finishing pass to the hot-saws is not the same for the several mills. This time for mill D is about half that for mills A, B and C, while the ratio of distances is roughly: $A = 4$, $B = 5$, $C = 3$ and $D = 1$ for the positions at which temperature measurements were taken. Two of the mills, A and B, used one saw and the others four saws. For the former it was possible to measure the temperature of practically every rail, while for mills C and D the average temperature of the rail bar as it passed to the cut (for mill D, and after cutting for mill C) was measured. In mills A and B the blooms were not reheated and in C and D they were reheated before rolling into rails.

Measurements were also made, at each mill, of a series of ingot temperatures, observations being taken as the ingot entered the blooming mill and for each alternate pass. It was possible in some cases to take observations on rail bars from ingots the rolling temperatures of which have also been measured. Auxiliary temperature measurements were also made at mill A, including observations at the bloom shears, open-hearth, Bessemer and blast furnaces, before and during tapping, pouring into ingot molds, and the temperature of ingots at stripping and removing from soaking pits. All observations were taken without any interference with the regular operation of the mills, and no special arrangements or installations were

found necessary for manipulating the pyrometer apparatus.

An inspection of the data shows a practical uniformity among the several mills for the rolling temperatures of ingots for steel rails, the range being from 1080°C . (1975°F .) to 1140°C . (2085°F .). With the exception of the Bessemer of mill D, rolled at an average temperature of 1047°C . (1917°F .), there is no very considerable difference among the finishing temperatures of the rails as observed at the hot saws for the several mills, the range being about 880°C . (1615°F .) to 990°C . (1815°F .). Or, in other words, the four mills all finished their rails to within 50°C . of 935°C . (1715°F .) on the average, excepting the Bessemer of mill D. This temperature of 935°C . is 270°C . (520°F .) above the mean value, 665°C . (1230°F .) of the critical ranges of these rail steels.

As to the distribution of temperatures within the head of a cooling rail, the center of the head is some 50°C . (120°F .) to 60°C . hotter than the optical pyrometer reading at 935°C ., therefore, the center of the head is finished, on the average, at about 325°C . (615°F .) above the critical range for 100-lb. sections.

The data on finishing temperatures show several other facts of interest. For example, it is evident that it is a possible and easy operation to determine accurately the temperature of each rail length in succession as it arrives at the hot saw. From the measurements at mill A, the relative temperatures of rails differing in weight of section, rolled from ingots having closely the same weights and temperatures, are shown. Thus the average of the finishing temperatures of the top rails (A and D or A and C) from 100, 90 and 75-lb. sections were respectively, 988° , 976° , and 924°C ., and similarly for the others.

Chemical analyses and photomicrographic examinations were also made and the mechanical properties determined for a number of samples of rail the rolling of which had been observed. From a comparison of these not very numerous observations, there appears to be not a sufficient degree of correlation to warrant associating very specifically any of the characteristics defined by these three methods of examination, either with the temperatures of rolling here observed or with each other.

The history of the "shrinkage clause" in American rail specifications was carefully reviewed during the investigation. The American Society for Testing Materials in 1909 limited the shrinkage allowance on 100-lb. sections to $6\frac{3}{4}$ in. in 33 ft., or to an equivalent of 1947°F . (1064°C .) for open-hearth and 2055°F . (1124°C .) for Bessemer rails. This specification is still in force. The practice of the rail mills regarding the actual shrinkage used, as given by Selew in 1913, shows a minimum shrinkage allowance for rails of 100-lb. section of $5\frac{5}{8}$ in. (1705°F . for open-hearth) and a maximum of $6\frac{3}{4}$ in. (1947°F . for Bessemer), most of the mills using a shrinkage of $6\frac{5}{8}$ in. or over,

corresponding to finishing temperatures of 1920° F. or over for open-hearth rails.

As would be expected from the nature of the process of rolling, starting with blooms of a given weight and section, the rails of heavy section are generally finished at a higher temperature than those of light section, although this is not the practice for all mills. This is recognized in most specifications by allowing a shrinkage of "1/8 in. less for each 10-lb. decrease in section" (from say the 100-lb. section). This clause is equivalent to finishing 80-lb. rails at 50° F. lower temperatures than 100-lb. rails.

If it be considered desirable to finish rails of all sections at the same temperature, this could readily be accomplished in practice by starting with ingots (in a continuous mill) or with blooms (in a mill with reheated blooms) the temperatures of which have been adjusted before rolling into rails. On the whole, it would seem more logical, if the best possible product is desired, to finish the rails of heavy section at a lower temperature than those of light sections. It should perhaps be again emphasized at this point that it is not difficult to control rolling temperatures pyrometrically.

Concerning the shrinkage clause, it is apparent that an intelligent effort was made about 1901 to limit excessive rolling temperatures by endeavoring to define the maximum finishing temperature at about 1600 to 1750° F., but the methods of measuring temperatures then in vogue did not permit a suitable pyrometric control, so that recourse was had to the shrinkage of the rail at the hot saw to define the finishing temperature, although no account was then or has been since taken of the different contractions for various steels.

It would seem, moreover, that the value then generally assigned to the shrinkage (say from 1904) did not give an exact idea of the finishing temperature, and this shrinkage allowance, as finally adopted, is unduly high, due in part to pressure from the manufacturers. It will also be recalled that the present rolling practice in four representative mills is on the average some 500° F. or more above the recalescence region but well within the shrinkage specifications. The maximum finishing temperature allowed by the American Society for Testing Materials, 2055° F. (1124° C.), is above the temperature of rolling of many ingots for rails.

The consensus of opinion is to the effect that rails should not be finished too high above their critical region. Nevertheless many are actually finished at very much higher temperatures, and this under a clause in specifications originally drawn with the purpose to limit the maximum allowable finishing temperature to slightly above the critical range. It would appear therefore that the present "shrinkage clause" of such specifications as those of the American Society for

Testing Materials, for example, has no significance whatever.

In conclusion, it should be emphasized that the various series of observations recorded in this investigation are of but a preliminary nature and do not pretend to solve the question of the relations between temperature of rolling and the properties of rails. It would seem desirable to make a much more complete and comprehensive study of the various matters mentioned and of related questions than has hitherto been attempted, and on a scale commensurate with the importance to the community of the problem of sound rails.

AMERICAN WOOL NEEDS BETTER HANDLING.

A preliminary report of the investigation into the methods of marketing American wool, now being conducted by the United States Department of Agriculture, indicates that 10 to 20 per cent of the value of the crop is lost annually through the neglect of a few simple measures. Under existing conditions, when American and Australian wools lie side by side in the warehouse, the poor handling of American wools is so noticeable that the price is inevitably affected. This handicap would be removed to a great extent if all growers would agree to do four things: Sack ewe, lamb, and buck fleeces in separate sacks; shear black sheep separately and keep the fleeces separate; tie the fleeces with paper twine, which does not adhere to the wool; remove the tags or dung locks and put them in separate sacks, marked to show their contents.

Figures prepared by the Bureau of Statistics, and based on reports from 383 growers who sheared in 1913 a total of 2,269,005 sheep, show that at the present time about one-half of the flock owners sack ewe, lamb, and buck wool separately, about 60 per cent separate the black fleeces and tie with paper twine, and less than one-half put tags in separate sacks. It is pointed out, however, that the correspondents who took the trouble to answer the inquiries of the investigators, and from whose replies these statistics are compiled, presumably represent the more progressive element in the industry, and that if it were possible to obtain the facts from every wool-grower in the country the percentage of those using the improved methods would be found to be much lower.

In the opinion of the investigators the reforms already mentioned would be sufficient for the present to put American wool in a different light. Later it may be advisable to adopt the Australian methods of "skirting," or removing from the fleece the wool of the legs and belly, and grading before sacking, but this is not urged now.

THE SOLID NONMETALLIC IMPURITIES IN STEEL—SONIMS.*

By HENRY D. HIBBARD, Plainfield, N. J.

Various names, such as oxidation products, occluded slag, entrained slag, mechanically held impurities, entrained silicates, and others, have been used by different writers to designate the subject of this paper. To get the advantage of a short distinctive name for them, the writer has proposed the term sonim (plural sonims), which will be used herein. A sonim may be defined as a solid nonmetallic portion of matter existing as an impurity in metal. A piece of brick, clay or sand imbedded in metal would be considered as a foreign body and, therefore, not a sonim. Gases are not included within the scope of the definition.

OCCURRENCE AND COMPOSITION.

Sonims occur disseminated throughout the steel as cast, in all forms from the molecule up to the visible globules into which they collect in the process of elimination. In steels made by the oxidation processes—pneumatic and open hearth—sonims may be very important, as they are nearly always contained more or less plentifully in such steels.

Those who have studied and written about sonims heretofore have worked almost exclusively on finished steels, often ignoring the specific methods by which the steel was made. While the results obtained from such studies are valuable, they give limited help in determining the cause, effect or cure of the disease. The exact metallurgical history of the steel would assist, but it is seldom or never given.

The treatment of the sonims is a metallurgical problem. An ultimate analysis of the steel, accurate and complete as usually understood, might give no clue to their presence or absence. The eye, aided perhaps by magnifying means, detects sonims when they are in the form of globules, but even the microscope fails to show them when they approach molecules in size, though then their effect is greatest.

Sonims are chiefly oxides and silicates, with some sulphides, either introduced in the charge or resulting from the methods of manufacture. The oxides are those of iron, silicon, manganese, and perhaps of other elements that have been added. The silicates are usually subsilicates, having three or four molecules of base to one of silica, the bases being chiefly oxides of iron and manganese. Probably phosphide, silicide and sulphide of iron are metallic impurities which dissolve in the metal and are outside our subject. They act somewhat like carbide of iron when present in small quantities, raising the tensile strength.

What the chemist reports as silicon in steel may have existed there in silicide of iron, which in well-made steel, made by the solution method, does good by favoring solidity; or it may have been in the form of silica, either alone or as a silicate. The presence

of 0.01 per cent of silicon may mean about 0.02 per cent of silica, or 0.10 per cent of a subsilicate of iron or manganese ($3 R O, Si O_2$). This silicate, having a specific gravity about half that of iron, will represent sonims of 0.2 per cent of the volume of the steel. This amount or even less when existing in certain ways considered later, may account for almost any degree of poor quality in the steel. Of course, sonims are directly due to the oxygen or oxide of iron absorbed by the metal in the process of manufacture, but they are developed in large part by the means employed to remove such oxygen. That is, when metallic manganese is added to oxidized iron containing the very harmful oxide of iron and silicon, another impurity, oxide of manganese is produced which has an affinity for the other two and all three unite in due course in a fusible silicate.

Any metal electropositive to iron at steelmaking temperature, such as calcium or manganese, which may be added to the steel, will probably be represented in the sonims by its oxide, silicate or sulphide, whether added for purifying or for giving certain properties to the finished steel. Any electronegative metal added, such as nickel and copper, will be practically all retained in metallic form in the steel.

The number of possible mixtures or combinations of these sonim-ingredients is seen to be very large.

Sonims may be considered as normal constituents, consisting of impurities separating from the steel on their way to join the slag.

SCUM ON INGOTS.

When soft steel of a commercial quality, made by what I have elsewhere styled "evolution" method, in which the gases are encouraged to evolve freely during solidification, is in the molds, there is a very active escape of myriads of small gas-bubbles, which, in rising, stir the metal very thoroughly, until it freezes or becomes pasty. During this evolution of gas a nonmetallic slag-like scum, more fusible than the metal, collects on the top of the ingot. In the acid open-hearth process it is sometimes olive-green or gray, though it may be black; and it is sometimes crystalline, though usually vitreous. On basic ingots it is black and crystalline.

Table I gives analyses of some of these scums, which show clearly that they are not a part of the slag. These samples were vitiated by dirt, clay, and refractory materials, which got into the molds in various ways and were dissolved by the scum; and as a consequence, the silica and alumina are too high.

TABLE I.—ANALYSES OF SCUM OF SONIMS FROM INGOT-TOPS.

	Acid Bessemer pipe-steel, first ingot.	Acid open-hearth boiler steel.	Basic open-hearth boiler steel.
	Per cent		
Iron (Fe).....	15.96	15.35	
Silica (SiO).....	7.95	20.38	17.44
Phosphorus	0.043	Trace	0.03
Manganese	38.66	48.50	36.00
Alumina		4.00	15.08
Sulphur	2.51	0.39	0.16
Lime (CaO).....			2.04

*Paper presented at 6th Congress International Association for Testing Material.

The quantity of this scum may be seen to increase after teeming has ceased, so further additions to it can only come from the metal. The final amount may be from 4 to 8 oz. per ton of steel or even more. This substance is, without doubt, chiefly sonims remaining in the steel when teemed. Their normal behavior in practice is considered elsewhere.

The elimination of phosphorus and particularly of sulphur from acid steel shown in these analyses is interesting.

Scum sometimes collects on the tops of high-carbon ingots—those which do not pipe but the metal of which is kept in some motion by escaping bubbles.

When drillings taken from a testpiece of an unfinished decarbonized open-hearth charge are being dissolved in 1.2 sp. gr. nitric acid, close observation will discover small quantities of minute black particles, separating from the dissolving metal. After a long series of observations, in which the charges known to be over-oxidized showed more of these particles than others, I came to consider them as iron oxide (Fe O) and to judge from their quantity of the degree of oxidation of the metal.

Rail-steel ingots examined within the past year or two at Watertown Arsenal showed numerous sonim globules within 1 inch of the bottom of the ingot, and far fewer, perhaps not over a fifth as many, 6 inches from the bottom, where the steel had remained liquid about 15 minutes longer. It was Bessemer steel made by a quasi-solution method, the ingots showing many blow holes; but there must have been little or no agitation after the steel had become quiet in the molds, and the relative freedom of the metal from sonims 6 inches from the bottom surface must have been due to the period during which the metal was still liquid, and the sonim globules were floating upward, to collect in or about the pipe and central segregation, adding to the injury from those defects. These globules must have largely been formed in the steel before it was run into the mold, and the whole mass must have contained sonim globules as plentifully as the metal in the outer skin of the ingots. The sonim globules, while very numerous, were not absolutely ruinous to the steel; and their effect in the interior away from the skin, where their quantity was greatly reduced, might be considered almost negligible, except in the upper central part of the ingot where they collected.

By hot working the sonim globules are of course drawn out with the metal into streaks and threads.

EFFECTS OF SONIMS.

The effects of sonims may vary in all degrees. They may be rank poisons, such that the thousandth part of the damage they work would render the steel unfit for any purpose whatever for which steel is required; or they may be comparatively harmless. Their effect is practically never proportioned to their quantity, but depends on the state in which they exist. Until much more is known about them, but

little can be said quantitatively of their effect on the finished product. Their ill effects are manifested at both ordinary and hotworking temperatures, but more strikingly in the latter, in the redshortness they cause. We cannot follow them back to their beginnings and, therefore, cannot say whether their first effects are produced in a physical or chemical way, but in their visible forms their effect is purely physical.

The experiment now described illustrates as an extreme example the overwhelming effect sonims may have on steel.

About 25 years ago I made in a Siemens furnace a heat of straight silicon steel, adding about 0.3 per cent of silicon and carbon at the end with no manganese. It was a 12-ton heat, the charge was pig and scrap, and no ore was added. The fuel was producer gas. The heat was normal until the addition of the ferro-silicon at the end, when the boiling ceased and the metal was cast into 12x12 ingots, flowing smoothly like milk. It lay dead in the molds and solidified quietly, forming the usual pipe. When reheated and rolled it proved to be redshort to a most astonishing degree, being broken up by one pass through the blooming mill perhaps as completely as if it had been made wholly of slag, or of sonims. It seemed evident that the redshortness of this steel was largely due to the reaction between the silicon added and the oxygen of the metal forming silica, which floated in the liquid steel as so much foreign matter very intimately intermixed, breaking everywhere the continuity of the metal, with the result that it could not be hotworked in the slightest degree without rupture. Manganese works to remove silica as well as oxide of iron from an oxidized iron charge.

The effect of a small amount of silica and oxide of iron was shown in this experiment to be extremely great. As the solidifying effect of the silicon added seemed to be about as great as if accompanied by the usual manganese, it seems fair to assume that a small fraction, probably less than a fifth of it, or say not over 0.06 per cent, was oxidized, and the resulting 0.12 per cent of silica with the small amount of oxide of iron left unreduced by the silicon was the cause of the excessive degree of redshortness. Therefore, a proportion of these sonims so small as to be much less than would be detected by the usual analysis is apparently enough in certain forms to destroy the usefulness of the steel. Chemists do not usually report less than 0.005 per cent of silicon, but, judged from its effect in the experimental heat, the tenth part of that percentage in the form in which it existed would have made the steel ruinously redshort.

Sonims in a far milder form but still one in which they worked important harm are next described.

After having had some experience at melting steel by the pig-and-scrap method, in which no ore was added to the bath, I was obliged, at another place, to make steel by the excess-of-pig-and-scrap method, the

excess of silicon and carbon being worked out with ore, a practice which requires methods quite different from those presented by the pig-and-scrap method proper. I was melting soft steel for boiler and ship-plate, and the plates made were passing inspection with some success; but they showed a tendency to redshortness, and some had "snakes" on the surface, while the elongation in the pulling test was usually close to the lower limit permissible when the plates were sold on specifications. The only thing unusual in the analysis was high silicon, ranging sometimes as high as 0.02 or 0.03 per cent.

Concluding, perhaps naturally, that the silicon was the cause of the trouble. I tried to eliminate it more completely from the metal of the next heats by oxidizing it with more plentiful additions of iron ore. To my surprise the chemist reported higher silicon than before; and the quality of the steel, as developed in rolling and testing, was worse instead of better. As usual in such cases, I questioned the accuracy of the analysis; but the chemist stood his ground, and events proved that he was right.

The next procedure was, of course, to go in the opposite direction; to use ore less freely and to allow time at the end for some of the iron oxide in the slag to be worked out by reduction and combination with silica of the acid hearth, the sonims in the metal being worked out at the same time. The oxides in the slag and metal followed similar courses as though there were some balance between them, that in the metal varying roughly with that in the slag.

The quality of the steel was improved by this procedure; and, on our going the same way to the reasonable limit, all signs of redshortness and "snakes" disappeared, and the plates scaled cleanly and freely in rolling, which they had not done before, even when they were not pitted (a defect due to other causes). The elongation in the pulling-test went up also. It thus became clear that, so long as there was manganese remaining in the metal, it was continually being oxidized, and the resulting oxide united with the silica as it formed, making a fusible silicate which collected together and floated out, collecting other oxides as it went, cleaning the metal, and eventually joining the slag. But after the manganese was all gone the silica formed floated in the bath unfused and therefore without power to collect into particles large enough to float on the top. Hence, when the oxidizing-conditions were intensified by larger additions of ore, the manganese was eliminated earlier than before, and the silica remained in larger quantity in the metal. In other words, the elimination of silica was seriously checked as soon as there was no manganese oxide to flux it within the mass of the metal; and it apparently remained suspended as so much foreign matter in the steel.

Another effect, possible of sonims, appeared about the same time in acid spring steel made by the melt-and-tap method in which as soon as the charge had

the desired carbon and temperature it received its final manganese and was tapped. Customers complained that the springs took a permanent set too quickly, and the defect was remedied in subsequent heats by adding more pig-iron to increase the carbon content a little and then holding the charge after melting and allowing it to boil and "work out," which would slowly remove carbon and sonims too, unless the slag was unduly charged with oxide of iron.

It is not easy to comprehend how a non-metallic ingredient could affect the hardening and tempering susceptibility, and the trouble may have been due to other causes, either gases or metallic impurities; but the fact that it yielded to the same treatment may justify its mention here.

In relatively large globules, the effect of sonims, unless their number be abnormally large, is not very important in the commoner grades of steel. An exception to the latter statement is sometimes presented when an extraordinarily large globule or group of globules has formed, which for some reason has not floated out of the metal, and which may, when extended by forging or rolling, form a weak spot or surface in the resulting article, which is a flaw, and may lead to rupture in service. Apart from such exceptional globules, which may reach 1/16 in. in diameter, sonim globules are rarely more than 0.01 in. in diameter, and may exist in any size from that down to single molecules, of which millions are required to make a globule 0.01 in. thick.

Both chemistry and microscopy may fail to determine the presence and amount of sonims in finished steel, when they are in their smallest and most hurtful forms. The mysterious lack of quality of certain steels may perhaps be explained by the presence of sonims, particularly steels made by the oxidation (Bessemer and open-hearth) processes. It has been common to ascribe chiefly or solely to the presence of oxygen in the steel such of their effects as have been recognized. With the control and elimination of sonims to the proper degree, steel-making will make a long step towards being an exact art.

Discrepancies are continually found between the physical properties of steels of substantially identical composition, made by the same process, the same plant, and the same men, and commercially of good quality. Differences occur in the properties of steels due to the different processes by which they were made, and abnormal heats are met with, having properties which do not nearly coincide with what would be expected from their analyses.

We are accustomed to ascribe such variations partly to be unavoidable inaccuracy of our determination of composition by the analyses of samples or drillings; partly to segregation; and partly to the temperature and other features of mechanical treatment. To this list of possible causes, I think one more may be added—namely, the presence, condition, and distribution of the sonims at the time of solidification.

To put the matter in another way: There are certain perfect physical properties which belong to a perfect piece of steel (which, strictly speaking, cannot be made) of any given composition, as the term "composition" is usually understood; but in practice each piece of steel of that analyses falls short of those perfect properties to some extent, according as it is better or worse made. All steels have defects in some degree, and one of the causes is often the presence of sonims.

To consider the effect of sonims as affected by their size, let us take a piece of steel containing a sonim globule 0.01 in. in diameter to each square inch of cross-section, the steel having a normal tensile strength of 60,000 lbs. per sq. in. The globule in question will have an area of cross-section of about $1/12,000$ part of the square inch, and, by displacing that amount of steel, will reduce the tensile strength about 5 lbs. per sq. in.—a wholly inconsiderable amount. A hundred such globules per square inch would decrease the tensile strength only about 500 lbs. per sq. in. Therefore a few sonim globules of that size may have a negligible effect.

What the sonims represented by the 0.01 per cent of silicon which seriously affected the physical properties of the ship-plate above referred to, were, and how they were distributed in the steel, is of course a matter of conjecture; but it seems plausible to conclude that their greater effect may have been due in some degree to their existing in smaller particles and in some particular manner of distribution throughout the steel.

There are two ways in which a given percentage of sonims may have a greater effect when the individual particles are of smaller size. One is, that the smaller particles, if globes or other regular geometrical figures, will have a greater aggregate area of cross-section per unit of volume or weight than larger particles, according to the geometrical rule that the volumes of similar solids are proportional to the cubes while the areas of their cross-sections are proportional to the squares of their homologous dimensions. The other and probably more important way is that the sonims when very small may be located largely along the contact-surfaces of the grains formed when the steel solidified, in which positions they would evidently cause weakness and reduce greatly the tensile strength and ductility. Larger sonim globules, which have been under motion due to gravitation, seem to be located at random throughout the steel, except that they are sometimes frozen in the act of collecting into clusters near the center of the mass.

When silicon is high, i. e., over 0.01 per cent in soft steel, it is likely to be largely in the form of oxide or silicate.

A very little sonim on the wall of a blow-hole will prevent the welding-up of that hole in rolling or forging.

THE ELIMINATION OF SONIMS.

In molten decarbonized iron prepared in the converter or Siemens furnace there may be existing in the solid state any or all of the sonims silica, oxide of iron and oxide of manganese; and in the fused state some of the silicates of iron and manganese. The infusible oxides are probably floating or suspended as minute particles too small for gravity to affect appreciably, much as finely powdered silica and iron ore will float in water making it turbid, though with the difference that the steel does not wet such suspended matter.

The sonims at this stage have little or no power to flux each other, or to unite and form globules of larger mass. They are so thoroughly disseminated in the iron of the charge that they seem to act almost as if in solution, but are made insoluble or precipitated by the added manganese, the effect of which is to change their composition and lower their fusion points, whereupon they proceed to agglomerate and escape from the metal. This is the usual way of eliminating sonims, and if the addition of manganese be large enough and sufficient time be allowed after its addition before teeming the result may be tolerable as to the properties of the product.

In molten steel ready for teeming, as in the ladle, there may be the same sonims as in the decarbonized iron, but in very different proportions and conditions. They should all have become fused or fluxed and have been for the most part eliminated. Such gaseous impurities as are contained should be held more securely in solution than before the final additions.

In the solidified steel ingot or casting there should be still less of the sonims than in the steel in the ladle. Such gases as have not been worked out or kept in solution will have formed blow-holes in the steel.

Let us first follow the course of the silicates, which are perhaps the most deleterious of the sonims. The oxide of manganese formed by the reaction of a part of the manganese added with a part of the oxide of iron (with the formation of FeO) fluxes the silica, forming a fusible silicate, the particles of which wet and join with other when they touch, making larger and larger particles. The molten metal and sonims do not "mix" any more than oil and water, nor do the fused sulphides mix with either. The silica seems not to be able of itself to split up oxide of iron so as to combine with the FeO resulting. Nor does metallic iron seem to be able to reduce Fe_3O_4 to FeO as manganese does. At all events the iron oxide lacks for some reason the power which oxide of manganese in molten steel possesses to flux silica. When silica is high in soft steel it is often, if not usually, accompanied by high oxide of iron, while if they fluxed each other only one of them—the one in excess—could be high.

The agglomerating-operation continues until the particles are large enough to be affected by gravity

and to rise toward the top of the metal. Each fused sonim globule also wets any other similar particle which it touches in its travels, and unites with it to form a large particle. Oxides unite with oxides and sulphides with sulphides.

The sulphide of iron is a dissolved impurity whose chief harm seems to come from weakness imparted when hot, thus causing redshortness in the steel. When metallic manganese comes in contact with the sulphide of iron it takes the sulphur from the iron, forming fusible and also insoluble sulphide of manganese, which is precipitated and at once begins to collect into particles which grow in size as they join with others of the same composition, until they reach the top of the metal, or until the steel has solidified sufficiently to prevent their further motion within its mass. This perhaps explains why there are at times discrepancies in the degree of redshortness displayed by different steels having high sulphur and of about the same percentage. Apparently as in the case of silicates the finely disseminated sulphides of iron and manganese are far more injurious than the same quantity in the form of visible particles. True, it would be difficult at present to discriminate between redshortness due to the various sonims, but it is not necessary as long as they all have similar effects and are amenable to the same treatment, that is, addition of manganese with allowance of time and gentle agitation.

This is another instance of the way in which an ultimate analysis of steel may fail to explain as much as it apparently should. The total sulphur in the steel may be unchanged by the addition of manganese, while its form may be, and its effect may thereby be, lessened in a most important degree.

If sonims do not wet each other, agitation will tend to retard their separation except (usually to a small degree) in the presence of a little manganese in the metal, or of an acid slag. Therefore, stirring before the final additions, though useful to dislodge dissolved gases is usually of slight effect in cleaning the metal of sonims. The exceptions to the above statement about stirring may, of course, be so emphasized as to be sufficiently effective. That is, an amount of manganese which would be small compared with that in the final additions, or a strongly acid vitreous slag, or both together, would be effective, given enough time or agitation or both. The time is required for the reaction to be completed, and after that, for the sonims formed by those reactions to escape from the metal.

In the low-carbon "evolution" steel which has been considered, the stirring which results from the escape of the gas-bubbles helps greatly the escape of the sonims which are then in the state of fusion and which continue to rise and enter the scum until the metal becomes too pasty or solid. The sonims which escape in the mold come chiefly from the interior parts of the ingot, which have remained molten longer than the metal near the outer surface. The latter congeals

before the sonims have had time to collect and rise as completely as those in the interior parts.

In pneumatic-process steel, as commonly made, the elimination, such as it is, takes place in the ladle and molds, though when recarbonized in the vessel a large part of the sonims are eliminated there.

When steel is "killed" so that it lies dead in the furnace, ladle, and molds, the conditions are in a sense unfavorable to the further riddance of sonims, because of the lack of agitation. Time will, of course, permit the floating to the top of any globules of sufficient size; but the formation of globules from the finely-divided sonims will proceed very slowly in dead steel. Stirring is as efficacious in agglomerating the fused sonims as it is in completing the reaction and collecting the precipitate in any other chemical operation. On such dead steel made by what I have termed elsewhere the "solution" method, in which the escape of gas during freezing is nearly or quite prevented, no scum rises to the top of the ingot; and any sonims in the metal will remain there, though they will be unequally distributed throughout the ingot, similarly to the segregated elements, as in the case of the Watertown ingots already noticed.

When the final additions to a charge of steel are made in the ladle, the conditions are unfavorable for the complete elimination of the sonims, though merchantable steel is made by following that plan. The most that can be hoped for is to reduce their quantity to tolerable limits and to have those present in the less hurtful form of relatively large globules. The time is limited in that case to the period which may elapse before the metal becomes too cold to cast successfully; while the average depth of metal through which a particle of sonims must rise in order that the metal may be rid of it is several times greater than that of the charge in the furnace. If it be argued that, because of the great mass of a 50-ton heat, ample time may be allowed for the escape of the sonims, this greater depth of metal must be remembered, and the greater distance the entrained matter must travel to reach the slag. The greater depth is not of course proportioned to the weight of charge; but it cuts down in a considerable degree the cleansing of the metal due to lapse of time after the final additions.

In the basic open-hearth furnace, the sonims may be eliminated by allowing time for the charge to work, and by having a slag low in iron; but greater care will be required than in the case of the acid open-hearth. There is one feature of the basic process, however, which aids their continuous elimination, namely, the reduction of metallic manganese from the slag by the carbon of the bath, the manganese entering in steel. This is never found to happen with acid steel. With the latter, once the manganese was all oxidized and eliminated from the metal, I never found it there until it was added in metallic form.

The practice of some steelmakers of adding a part of the manganese some time before tapping, and the

remainder immediately before, or in the ladle, undoubtedly has an effect in eliminating the sonims by allowing more time for them to get into the slag after forming. Somewhat similar, in a lesser degree, is the practice of adding a part of the scrap to the molten bath. The resulting agitation, and the action of the manganese of the scrap, will cause early formation of fusible sonims, and therefore their removal.

Sonims are, and have been, commercially eliminated from steels in regular practice with tolerable results, even if the theory of the methods used has not been fully understood. "Working out," "shaking down," and similar furnace-practices, as well as the final addition of manganese, are measures whose chief effect, aside from giving the steel the desired composition, is to allow or facilitate the elimination of sonims from the metal. The various processes afford different degrees of completeness in the elimination of the sonims.

Well-made crucible steel should be the freest from sonims; electric steel next; then acid open-hearth steel finished in the furnace; and finally open-hearth and Bessemer steel made in the ladle.

In the first three processes named the practically complete removal of the sonims is possible, though it may be said not to be usual. In the absence of definite information as to what good slower driving would do, commercial reasons, or the demand for a maximum output at a minimum cost, usually outweigh the tendency to clean up the metal to the greatest practicable extent, and will continue to do so, at least, until proper specifications for sonims based on their proved effect are made and enforced.

In the crucible and electric steel processes there are or should be no final additions for the purpose of deoxidizing the metal; and therefore there will not be formed, late in the history of the charge, any sonims which would have to be largely eliminated to secure the highest quality of product.

CONCLUSION.

In the absence of fuller knowledge of sonims, and their effect on steel, it is hardly proper to make specifications regarding them. Of course, to fill usual requirements as to elongation, reduction of area and clean surface free from checks and seams, demands that sonims be kept within limits. Generally speaking, from steel which is free from redshortness when rolled or forged, and which meets the usual physical test requirements for structural steel, the sonims will have been eliminated to a reasonable degree and those present are collected into visible globules when the steel solidified. In the finer grades of steel, and particularly in tool steel, the elimination of sonims should be much more nearly complete.

A series of patents are now issuing covering various means of freeing steel of its sonims, some of which are based on methods long since well-known to steel makers.

ELECTRIC ZINC SMELTING.*

By W. R. INGALLS.

The idea of electric zinc smelting is no new thing; nor is it still merely in the laboratory stage. For several years a considerable tonnage of electrically smelted spelter has been produced commercially in Sweden and Norway. In 1911 there was a production there of 6,575 long tons, in 1912 of 8,000 tons; in 1913 it will be larger.¹ Although I have no detailed information about this, I am under the impression that the larger part of this spelter is derived from re-smelting dross, scrap, etc. However, some of it is derived directly from ore.

I shall not go into the historical phase of this subject any more than is necessary to give a little perspective. The Cowles brothers first tried the electric smelting of zinc ore about 1884, but were diverted into the field of aluminum. DeLaval, the distinguished Swedish inventor, about 1898 took out patents on his well-known arc furnace, which is depicted in many text-books, and tried it in Sweden about 1901, since which time works have been running at Sarpsborg and Trollhättan more or less continuously. Also there is a plant at Ihlen, near Trondhjem.

According to the report of the Hydraulic Power & Smelting Co. on Nov. 4, 1913, the capacity of the works at Sarpsborg had been increased from 8,000 to 10,000 tons per annum. Erection of a new zinc smelting works at Trollhättan is proceeding as rapidly as possible. At the present time, of the seventeen 1,000-h. p. furnaces and eight 500-h. p. furnaces to be installed, thirteen of the former and all of the latter are completed. (The 500-h. p. furnace has probably a daily capacity of about four tons of ore, and the 1,000-h. p. furnaces twice as much.) The company goes on to say in its report that its furnaces have been running on the ordinary classes of roasted ore, which have not yet proved commercially profitable. Considerable progress is, however, being made, and the results achieved in August, 1913, were a great improvement over any previous month.

Since 1901 there have been many patents taken out by many experimenters, and several ambitious experiments have been made, most of which have been disappointing. Although electric smelting has been commercially carried on in Scandinavia, the measure of its success is doubtful, and certainly metallurgical difficulties have been experienced which would prohibit the Scandinavian processes almost anywhere else. The same metallurgical difficulties have been experienced by other experimenters.

Nor shall I enter upon any remarks reviewing the deficiencies of the ordinary process of fire smelting and the hypothetical advantages of electric smelting, which have been recited as a panacea for previous ills.

*Paper read at a meeting of the New York Section, Nov. 20, 1913, in joint session with the Am. Inst. of Mining Engineers, and discussed at the 25th General Meeting of the American Electrochemical Society, in New York City, April 16-18, 1914.

¹Statistics published in January, 1914, give 17,000 tons for 1913.

The ideas about smelting zinc ore in a large instead of in a small retort, of generating the heat exactly in the place where it is needed, of substituting a continuous operation for an intermittent one, are engaging, each and all of them, but let us first consider just what these ideas involve.

An early metallurgical difficulty was the proper condensation of the zinc. Spelter was wanted; blue powder was got. I use the term "spelter" as meaning zinc condensed in molten form. The condensation of the zinc as blue powder in whole or in large part was a bar to success. Until we were able to leap that hurdle there was not much use in thinking of the other obstacles. If, as at Trollhättan, it were necessary to re-smelt two tons of blue powder with every ton of ore, the energy required would be prohibitive except in places where power is available at a phenomenally low figure. Many investigators of this subject have considered the trouble in condensing the zinc vapor in the right way to be in the condensing apparatus. I shall indicate further on that the trouble really originates in the furnace itself, and is not very much a matter of the condenser; that, given the right conditions in the furnace, condensation is effected without any special difficulty. Before going further into this subject it is well to reflect upon the inherent differences of electric smelting, or what we hope to make of electric smelting, and the ordinary practice in smelting, to which, for convenience, I shall refer as fire smelting.

Fire smelting as ordinarily practiced is a two-stage intermittent process. The retorts are charged and are then slowly heated. Hydrocarbons are driven off, carbonates are decomposed, and preliminary reductions are effected in the charge. During this stage the gas, high in carbon dioxide, burns with a violet flame at the end of the condenser. The second stage is the stage of zinc reduction and distillation. When it is completed the residues are discharged. The next day the same cycle of operations is repeated.

Electric smelting is aimed to be continuous, and many experimenters have contemplated doing everything in one operation. I do not believe that to be possible. Electric smelting can be made, in fact, is made, a continuous process, but it must be a two-stage process. Either the first stage of fire smelting must be done in a separate furnace, or the charge put directly into the electric furnace will yield blue powder. The blue powder must be re-smelted in order to get spelter, so we still have a two-stage process.

Assuming a properly preheated charge, what differences are there then between the internally electrically heated retorts and the externally fire-heated retorts?

In the former there are, among other things, (1) an absence of excess of carbon in the charge, (2) the ore is dropped upon very hot slag (in the case of some furnaces, at least), (3) there is possible exposure of the charge to excessive temperature, and (4) there are possible electrical effects.

Now we know that the reaction between zinc oxide and carbon monoxide is reversible. We know that in fire-smelting, blue powder is formed, especially in the earlier part of the distillation. We know that the retort gas is then relatively high in carbon dioxide. We know that subsequently the gas becomes almost pure carbon monoxide. We know that attempts to obtain zinc from the blast furnace have given only blue powder, because of oxidation by either carbon dioxide or oxygen.

Let me digress long enough to explain the nature of blue powder. There are two kinds, viz.: meltable and non-meltable. The meltable powder results from improper physical conditions. The non-meltable results from improper chemical conditions. This substance, which between the fingers appears to be an impalpable powder, when examined under the microscope is seen to consist of a myriad of little pellets, mostly spherical and coated more or less with some substance that prevents their coalescence. That substance may be zinc oxide, or may be something else. The pellets sometimes exhibit a frosted appearance, and sometimes show what look like minute white hairs.

In the metallurgical treatises, blue powder condensation is commonly ascribed to the condenser being too cold. That may account for the meltable blue powder, but how can it account for the oxidation exhibited by the non-meltable? Whence comes its oxygen but from carbon dioxide? The gas from electric furnaces operated without especial precautions is invariably high in carbon dioxide. The presence of that oxidizing and diluting gas is sufficient explanation of the formation of blue powder.

Carbon dioxide is not the only source of trouble, however. The essential condition of zinc condensation is purity of the gas and vapor. Impurities may be: (1) Carbon dioxide and other gases, (2) dust, (3) substances volatile at high temperatures. A step is gained when we recognize the causes of blue powder. Recognizing them, however, the avoidance of them is not entirely easy.

I am not going to describe or discuss at this time either processes or types of furnaces. Some European experimenters have worked on the line of a preliminary pyro-metallurgical concentration and the smelting of a collected zinc oxide fume. American experimenters generally have directed their attention to the direct smelting of ore and the elimination of gangue by scorification in the electric furnace itself. Among the furnaces we have those of the arc, arc-resistance and resistance types. Patent specifications show many freakish designs. Among the furnaces seriously tried there are such as the horizontal cylinders of Queneau, Specketer and Weeks, the radiation furnaces of De Laval, and FitzGerald & Thomson, and the pot furnaces of Cote-Pierron, Salguès, Johnson and others. Reduced to their elements, there is no fundamental difference among them.

I have touched, in this discourse, only upon the high

points of the subject, and have conveyed the impression, I hope, that we are very far from knowing all that we need to, even in respect to them. I shall indicate that we know still less in trying to answer the question: What warrant is there for the widespread attention to electric smelting and the large sums of money that are being spent in trying it? My answer to that question is that not even yet have we much beyond visions and ideas. We have very few facts and conclusive figures. Electric smelting is one of the relatively unexplored fields of metallurgy, and is attractive because of its mystery, if nothing else. Among our visions we conceive the possibilities of smelting certain kinds of ore that are extremely troublesome or even impossible in the fire-smelting process. The range of such ores is much less today than only a few years ago, but we still find difficulties with ores containing a fluorspar gangue, with sulphide ores that are very high in isomorphous iron, and with those ores that are cryptocrystalline mixtures of component sulphides. There is, moreover, the possibility of increasing the extraction of zinc, and especially is there a possibility of increasing the extraction of the lead and silver content of zinc ore, from which our present methods secure too small a proportion, perhaps not more than five-eighths from each, if I may venture upon a generalization.

Recognizing that electric zinc smelting is a performable process, the question of importance is the economy of the process, in other words, the cost of performing it. Let me make haste to say that, in the case of those ores from which a recovery of lead and silver, besides zinc, is expected, we should make comparison with the cost of the total process as ordinarily conducted, that is, the extraction of zinc and the subsequent extraction of the lead and silver from the residuum. Unfortunately we do not yet possess the data that warrant us in coming to any firm opinion respecting the cost of electric smelting.

A crucial point is the matter of energy, which in the process of fire smelting is used in the form of coal, and in the electrical process in the form of electric current. In the smelting of 1,000 kg. of zinc ore, of about 25 to 50 per cent zinc content, it is estimated that from 900 to 1,050 ton calories of heat are necessary, which is equivalent to 1,047 to 1,221 kw. hours of electric energy. In mentioning these figures, I mean, of course, to make a broad generalization, a translation of energy from terms of heat to terms electrical. If the electric smelting process be conducted as a two-stage process, where preliminary reactions are effected in an auxiliary furnace fired with coal, as Mr. Johnson does, and this partially-reduced hot charge be delivered to the electric furnace, the power required in the latter will naturally be diminished. No doubt this is a proper direction in which to work, that is, to use the cheaper energy of coal wherever it can be used and confine the more costly electric energy to work for which it is especially needed. On the basis

of an estimate of 1,200 kw. hours, it will readily be seen that, under any conditions of power supply that we know of in this country, the power cost of reducing a ton of ore will be more than the coal cost. By just so much as the use of electricity can be limited, by just so much will the balance swing in its favor.

Comparing fire smelting and electric smelting, with respect to the items of administration, general expense and yard labor, we may expect about the same costs in the one process as in the other. In the matter of roasting we may admit some economy in favor of the electric smelting process, inasmuch as the ore for that process may not have to be desulphurized so completely as in the ordinary process; indeed, we may not want to desulphurize it so completely. The consumption of reduction coal is undoubtedly in favor of the electric furnace. We cannot, in the electric furnace, use the same proportion that we do in the ordinary furnace, even if we should want to. Setting the consumption of electrodes against the consumption of retorts, we cannot yet safely say which will be the more costly. It has been argued at considerable length that electrodes will be very much cheaper than the retorts of the ordinary furnace. The exponents of that idea may be right. I say only that at the present time we do not know, and in the only extensive work in electric smelting that we know of, the work in Scandinavia, the cost of electrodes has been higher than the cost of retorts in the ordinary process as practiced elsewhere in Europe.

The matter of labor cost is also quite uncertain. At first sight one is apt to jump to the conclusion that, in running an electric furnace of three or five tons' daily capacity, the labor cost would be much lower than in our present furnaces in which we have small retorts. That may be so; at present we only surmise. It may be overlooked that in our present furnaces the organization of labor is highly developed. The maneuver requiring the most labor is concentrated in a few hours, and during the remainder of the 24 hours a few men attend to a big furnace comprising a great many retorts. Anyway, at Trollhättan the labor cost in 1911 was more than in ordinary fire smelting elsewhere in Europe. As to repairs and renewals in electric smelting we know next to nothing. In the matter of capital charges I think it is not unlikely that the electric plant will have a little advantage, that is, if it be not charged with the cost of electric installation, which, of course, would be improper, because that has already been reckoned in in considering the cost of electric energy.

Summarizing, if the unit quantities of materials used in Sweden and Norway be multiplied by American costs, especially those of the region west of the Rocky Mountains, the total cost of the application of the process used there would be prohibitive. The whole subject of electric smelting is in its infancy. Yet it is possible that ways around some of the difficulties that we now see, including those pertaining to matters of

cost, may be found, and that in the end we shall in one way or another be able to see some advantage in electric smelting. Anyway, it is a subject that is worth the work that is being put into it.

THE EXTENT OF MINERAL WASTE.*

It is a reasonable estimate that the present waste, in large measure unnecessary, of mineral resources amounts to a national loss of not less than \$1,000,000 a day.

In one respect at least a consideration of the mineral wastes has a basis quite different from the consideration of agricultural wastes. Our crops represent an annual production from a reasonably permanent soil; our forests may grow again, though a much longer period of time is required; and the soils themselves may be reproduced from the subsoil and the rock beneath. But of our mineral resources we have only the one supply. This supply is to a considerable extent destroyed in use; and at the present increasing rate at which we are using and wasting it our one supply will be either exhausted or largely depleted while the Nation is yet in its youth.

The most urgent need for investigation and reform is in connection with the unnecessary waste of oil and natural gas that still prevails in many parts of the country. Even with the limited facilities at its disposal the bureau has been able during the current year to stop a waste of natural gas valued at not less than \$10,000,000, an amount that exceeds by six times the total cost of the bureau's investigations to date. There is urgent need of enlarged facilities with which to push this work more rapidly. A few years of further delay and this valuable source of national wealth will have been wasted—permanently lost.

The individual operators in causing this waste have followed their natural bent for temporary gain. The States have permitted this criminal waste without protest, fearing that interference might retard development. Will the National Government do the same? The saving already accomplished was the result of inquiries and researches that enabled the engineers of the bureau to demonstrate to the oil and gas men in one of the Oklahoma fields that much waste of gas could be prevented without stopping the drilling for oil.

If the funds at the disposal of the bureau had been large enough to provide for more extended investigations and demonstrations, the prevention of waste would have been much greater. As it is, however, in many parts of the Oklahoma oil and gas fields the waste of natural gas that still continues is equivalent to \$15,000,000 to \$20,000,000 per annum, and this waste in all of the oil and gas fields of the country now aggregates more than \$50,000,000 per annum. Of

the total waste of gas in the different oil fields of the country more than 80 per cent is believed to be easily preventable. As regards the remaining 20 per cent, it is believed that gasoline may be extracted from much of it and the gas itself burned for some useful purpose.

The need for enlarged investigation is further shown by the fact that in addition to this waste of gas the waste of petroleum, and especially the loss of the lighter oils, in pumping and storage is much greater than is ordinarily supposed. Moreover, the injury caused in a number of oil fields through the flooding of oil and gas strata by underground water is another phase of the subject calling urgently for inquiry and investigation.

It is estimated that the proposed investigations into the waste of oil and gas would cost from \$30,000 to \$40,000 per annum, and it is believed that the saving to the national wealth would be more than a hundred-fold for each dollar expended in such an investigation.

The waste in coal mining is another drain on our national wealth which calls for serious and extended inquiry and investigation. A preliminary estimate, based upon limited inquiry and examination, indicates an annual waste or loss of coal in mining and handling of not less than 250,000,000 tons per annum. This represents a loss from our best and most easily mined coals and those nearest our great centers of industry. What is needed in connection with this loss is a thorough underground survey and examination at certain carefully selected areas in each of the important coal fields of the country, with a view to determining the exact conditions under which mining operations take place and the possibilities of adopting less wasteful methods. With this large amount of accurate information laid before the public, it will then be possible to obtain the adoption of far less wasteful methods of mining. Such an investigation, thoroughly conducted, would cost about \$50,000 per annum for three or four years. It is confidently believed that the results of such an investigation would mean a saving in fuel resources having a value to the nation of considerably more than \$50,000,000 per annum.

There is need of similar investigations looking to a reduction in the wastes or losses in the mining, preparation, and treatment of our metalliferous ores and metals, which wastes and losses aggregate in different cases from 10 to 50 per cent of the total yearly production of such minerals and metals. A few of these wastes may be regarded as representing to some extent a deferred use of the materials. These it is not now proposed to investigate. Many others represent a total and permanent loss, and in the majority of our metals this reduction in our national supply will at no distant date become a serious problem. Certain investigations relating to both safety and waste in connection with our metal mining and metallurgical operations are already under way, but they are quite inadequate to meet the need for investigations in these branches of the mineral industry.

*From the Third Annual Report of the National Bureau of Mines Joseph A. Holmes, Director.

MANGANESE DEPOSITS IN THIS COUNTRY.

The United States Geological Survey has published, as Bulletin 427, a report on the manganese deposits of the United States, by E. C. Harder. The bulletin contains accounts of the geology and chemistry of the ores, the methods of mining, the uses of the metal, and the nature and extent of the industries to which it gives origin.

Manganese is obtained commercially from manganese ores, manganiferous iron and silver ores, and manganiferous residuum from zinc roasting. Manganese ores are found in many parts of the United States, but at only a few places do they occur in sufficient quantity to be of high commercial value. They have been mined in the New England, Appalachian, and Piedmont regions in the eastern United States, in northern Arkansas, and to a small extent in central-western California. Manganiferous iron and silver ores are also widely distributed. The iron ores have been mined for their manganese content in the New England, Appalachian, and Piedmont regions in the eastern United States, in northern Arkansas, and in a few localities in the Lake Superior district, and the silver ores in several western silver districts, principally Leadville.

Manganese mining has never been a very important industry in the United States, owing to the small extent and the discontinuous and scattered nature of most of the deposits. Nearly all the ore mined must be either washed or stored or both. Single pockets are of small extent and are soon exhausted, discouraging the erection of expensive concentrating plants.

Most of the manganese ore consumed in this country is imported from Brazil, India, and Cuba, smaller amounts being obtained from Russia, Germany, Great Britain, Belgium, Japan, the East Indies, and other countries. It is used largely in the manufacture of iron-manganese alloys, and these, together with the imported alloys, are consumed in steel manufacture. A considerable quantity of high-grade foreign ore is used in the manufacture of dry cells for electric batteries. Most of the domestic manganese ore, with perhaps a small portion of the imported ore, is used in the manufacture of brick and pottery as a coloring material or for other chemical purposes. Only a small portion of the domestic ore is used in steel manufacture. Manganiferous ores of iron and silver are used both in the manufacture of iron-manganese alloys and as a flux in smelting copper, lead, and silver ores.

The use of manganese in the arts is of great antiquity, having been known at least as long ago as the time of the ancient Egyptians. One of its first uses was in glass making. Egyptian and Roman glass-ware have been shown by analyses to contain over 2 per cent of manganous oxide. Pliny mentions the use by the Romans of manganese oxide, under the name "magnes" for decolorizing glass. He consid-

ered it a variety of lodestone or magnetic iron ore.

In the manufacture of steel manganese finds its greatest use. Manganese steel is used for dredger pins and other parts of dredging machinery; for dipper teeth of steam shovels; for parts of crushing and grinding machinery, such as shoes and crusher plates in ore mills; for ore chutes and screens; for elevator links, especially where the wear and tear is heavy; for agricultural implements, as plow shares and plow points, cultivator fingers, and even shovels, spades, rakes, hoes, and forks; for wheels, tires and axles on railway cars, street cars, and mining wagons; for cogwheels; for couplers between railway cars; for railroad and steel-car rails on curves; for burglar-proof safes; and for many other purposes. One of its most important uses at the present time, on account of its nonmagnetic property and hardness, is for cover plates and coil shields in large electromagnets, such as are used for clutches in lifting pig and scrap iron at foundries.

Estimates of pig-iron production in 1913, so far as available, are as follows: United States, 31,089,000 tons; Germany, 19,014,000 tons; the United Kingdom, 10,480,000 tons; and Belgium, 2,437,000 tons.

The combined output of steel in the United Kingdom, Germany, and the United States in 1912 exceeded 55,000,000 tons, and the world's output may be estimated at between 71,000,000 and 72,000,000 tons. The following statement shows the production of steel in the principal countries during 1910, 1911 and 1912 (the last year's figures being provisional):

Countries—	1910. Tons.	1911. Tons.	1912. Tons.
United States	26,095,000	23,676,000	31,251,000
Germany (including Luxemburg)	13,479,000	14,778,000	17,024,000
United Kingdom	6,470,000	6,565,000	6,903,000
Russia (excluding Finland)	3,479,000	3,870,000	4,416,000
France	3,450,000	3,775,000	4,333,000
Austria-Hungary	2,120,000	2,290,000	2,642,000
Belgium	1,914,000	2,157,000	2,475,000
Italy	720,000	724,000	903,000
Canada	734,000	788,000	^a 853,000
Sweden	464,000	463,000	507,000
Spain	367,000	282,000	(^b)
Bosnia and Herzegovina....	33,000	35,000	38,000

^a From Bulletin 9 of the American Iron and Steel Institute.
^b Not available.

Experiments conducted in the laboratory of the U. S. Geological Survey have shown that on igniting powdered alunite all the water and three-fourths of the sulphuric acid are driven off. When the residue is leached with water, potassium sulphate dissolves and insoluble alumina is left. The average quantity of potassium sulphate leached from the ignited mineral is 17.9 per cent of the original material used. As the coarsely crystallized alunite was found to contain 19.4 per cent of potassium sulphate, 92 per cent of the total potash present was obtained by simple ignition and subsequent leaching.

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NOTES AND COMMENTS.

Adulteration of Foods in Germany.

The following remarks on the subject of food adulteration in Germany are based on reports of Prussian State officials and were published in the *Zeitschrift fuer oeffentliche Chemie*:

The use of artificial butter grows from year to year; it is even being used in the country. In spite of this increasing consumption there is much uncleanness where it is produced, and there is great necessity for purifying the raw products used. Tallow is often confiscated because it contains hair, flies, splinters, and other foreign substances. The manufactured butter is also sometimes confiscated because it contains a large percentage of soda. Margarin manufacturers are still using benzoic acid and sulphuric acid as preservative agents. Up to the present the penalty for using such adulterants has not been clearly defined, because the law has not been properly explained. Mixtures of lard, beef fat, and artificial fats are often made. Vegetable fats are being more and more used especially in the form of hardened oils.

Flour and bakery products also need careful supervision, because of the mixture of inferior products, sand, weed seeds, and mites. In many districts it has been found that talcum was used to adulterate flour, and that there was uncleanness in the storerooms, and

in the manner of manufacture. Mites, worms, and spiders were found in the flour bins. So-called egg mixtures often resemble eggs only in color, and that is given by a coal-tar product. Fruit juices are also artificially colored—often with poisonous coloring matter.

In a sparkling fruit wine advertised as free from alcohol, 7 per cent of alcohol was found. The green color of canned vegetables was found frequently to be the result of the use of salts of copper. In one kilo (2.20 pounds), 132 grams (4.65 ounces) of copper salts were found. Marmalade and fruit jellies were found often to consist almost entirely of artificial ingredients. Coffee was most frequently adulterated with pulse or lupine seeds.

In many instances malt coffee was found to be simply unmalted, roasted barley. Adulterated vinegar is said to have caused two deaths. Wines were less impure owing to the strict supervision exercised over the wine industry, but in the manufacture of beer, much is to be desired in the matter of cleanliness. Twice brandy was found to be adulterated with methylated spirits. Lead was also used for coloring utensils and vessels in daily use. The above would lead us to believe that conditions in Germany are not so satisfactory as in this country, although Germany is usually cited as a nation where all commercial activities are closely supervised.

Artificially Hardened Oils in Competition With Copra Oil.

Oil pressed from copra, or the dried meats of the cocoanut, is solid at ordinary temperatures, the melting point being about 80° F. Copra oil has always been a favorite grease for fine hard soaps, and since the invention of certain refining processes about the year 1905 it is being more and more used as an ingredient of margarin. Oleo oil and neutral lard have been the standard hard ingredients for margarin, and still are in the United States. But in Europe copra oil is rapidly replacing the animal fats for this purpose, thus leaving a diminishing proportion for the soap makers, who must now resort more to animal fats. But owing to the world's shortage of animals, still further supplies of hard fats must be sought.

Artificially hardened liquid oils are now being supplied for this purpose in large quantities, both in Europe and in the United States. On account of the relatively lower price of linseed oil during the past year, this has been more generally hardened for the soap makers than the other oils. Whale oil is also coming into use for this purpose. Cottonseed oil, being relatively high in price, is not being hardened in important quantities except for edible uses. In the United States most of the large makers of compound lard, who formerly used 80 per cent of liquid cottonseed oil and 20 per cent oleo stearin, now use cottonseed oil exclusively, after hardening it to the desired consistency for artificial or "compound" lard. In Europe small quan-

tities of cottonseed oil are being hardened for margarin, and this will probably be an important business, but for the immediate present most of the hardened oils are being used for soap.

The Commercial Agent Erwin W. Thompson reports that the total capacity of European hardening plants for 1914 is put at 1,375,000 bbls. (400 lbs. each), but not more than half this amount was made in 1913. In the United States the output for 1913 is put at 500,000 bbls., and the plants are said to be rapidly increasing.

The composition of margarin in the principal producing countries of Europe is estimated for 1913 as follows (metric tons of 2,204.6 lbs.): Copra oil, 169,000; palm-kernel oil, 35,000; animal hard fats, 143,500; liquid oils, 150,000. The production of margarin is increasing year by year, and copra oil as an ingredient is becoming increasingly popular. The demand for this purpose alone will probably be 250,000 tons in 1914, and this is two-thirds of the world's crop. The soap trade will always require important quantities, because, aside from its mere hardness, copra oil possesses certain characteristics rendering it especially desirable in some kinds of soap, such as for use with sea water, and for shaving soap.

Despite all the artificially hardened oils, there seems no immediate likelihood of a surplus of copra oil. The copra crop of 1913 is estimated at 630,000 metric tons. At the highest probable yield of 60 per cent, this would make 372,000 metric tons of oil, or say 2,000,000 barrels. Although this is three times the crop of 1906, the admission of this oil to the edible class since that date has kept up and even advanced the price.

What Determines the Quality of Paper.

After discussing the fundamental properties of paper, such as thickness, strength, stretch, opacity and other physical and chemical properties entering into the make-up of a sheet of paper, Mr. Arthur D. Little continues by saying: "The number of factors which are concerned with the quality of paper in its multitudinous applications to special uses is so great as to prevent consideration or even enumeration of them all. A paper for wrapping hardware or a card for mounting silver jewelry may seem to possess every desirable property, and yet be worse than useless because of a trace of sulphur. A printing paper may develop "whiskers" or clog the type by mineral filler, a coated paper may pick or develop odor, a cigarette paper may burn badly, a writing paper may allow the ink to spread because the size has been converted into peptones by overheating, a filter paper may fail to hold a fine precipitate or unduly retard the passage of liquid, and so on. Enough has been said to suggest to consumers of paper the complexity of the problems involved in the determination of quality, the importance of paper testing, and the advantages to both maker and consumer of carefully considered and intelligently drawn specifications defining quality as a function of intended use."

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THE PHASE RULE AND ITS APPLICATIONS.

B. B. FREUD.

When Roozeboom took the Phase Rule of Willard Gibbs out of the field of mathematical physics and applied it to the classification of the different kinds of chemical equilibrium, he at the same time established its value and made it generally accessible. Meyerhoffer says: "The phase rule is one of the most comprehensive generalizations known to man. It is of unlimited application, and offers an accurate and ready means of classifying all states of physical and chemical equilibria." However, while its applicability is so general, it is not at present used as often as it should be outside of the field of physical chemistry. But it is gradually finding its way into the other branches of chemistry. Its recent applications in the interpretation of cooling curves and the determination of the composition of solid phases without analysis, in the study of blast furnace equilibria between iron, carbon monoxide, and carbon dioxide, and in the study of the ammonia-soda process, all show how it may be profitably applied. With its help we can classify any number of different isolated cases of equilibria; for instance, it can be used in the study of the conditions regulating the formation of alloys from mixtures of fused metals, or of the various salts in geologic formations, as well as the reactions of iron and carbon in the formation of steel.

With the hope of making the phase rule a more common tool in the hands of the chemist, this brief exposition of its meaning and application is written. Its ultimate object is to learn in how many different states a molecule may exist in equilibrium, and what changes a system may suffer without losing some of these states.

It is necessary first to define several terms commonly used in connection with this subject. The "components" of a system are those substances which take part in the reaction but which are not decomposed in the process. They are the chemical divisions of the system. They are those divisions whose compositions in each phase may be *independently* varied, those which are *indispensable* in describing each phase. A "phase" is each homogeneous state, solid, liquid, or gas, which the components can produce. The phases are the

physical states in which the components can exist. The "degree of freedom" or "variance" of a system is the number of independent variables which must be fixed before the state of the system can be rigorously defined. The "state" of a system may be defined by the intensity factors temperature, pressure, and concentration. For instance, the condition of equilibrium of a gas with respect to temperature, pressure, and volume is defined by $p_v = RT$, where R is a constant whose numerical value depends on the units employed. If but one of these three variables, say the volume, is fixed, the "state" of the system is undefined because the gas can have very different values for temperature and pressure and yet have the given value for v . Two of these three variables must be known before the state of the system is rigorously defined. If any two are definitely fixed, the third automatically assumes a definite value. The former are called the independent variables or the degrees of freedom, the latter is a dependent variable. The degree of freedom of a system is the number of independent variables that must be fixed in order to define the state of a system. Thus the gaseous system we have been considering is *bivariant*, it has two degrees of freedom.

Having defined the terms, we shall state the relationship between the number of components, the number of phases, and the degrees of freedom of a system which Gibbs discovered and which is the phase rule. The number of possible variations of concentration, pressure, and temperature, without changing the number of phases, is two more than the difference between the number of components and the number of phases. If F is the number of degrees of freedom, C the number of components, and P the number of phases, the equation

$$F = C - P + 2$$

is the statement of the phase rule.

To illustrate the application of the rule we will take the system, silver + copper. Hence $F = 2 - P + 2 = 4 - P$. There are, in this case, three intensity factors—temperature, pressure, and concentration. Our graph must therefore be in three dimensions. It is customary to plot concentration and temperature in the plane of the paper, and pressure at right angles to the paper. (See Fig. 1).

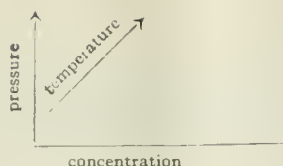


Fig. 1.

Our "curve" representing equilibrium between vapor and solid, vapor and solution, or vapor and solid and solution will be on a surface. The following figure, (Fig. 2) from Ewell, represents the surface representing equilibrium in the system Cu—Ag, as viewed from above the plane of the paper.

The lines OA, OB, OJ, OK, and ON divide the field into the several phases that are in equilibrium.

Consider the point D. Here there are 2 phases present, solution and vapor (since D is on the surface). Hence at D there are 2 degrees of freedom, since $F = 4 - 2$. If we use up one of these by keeping the concentration of the silver and copper constant, that is by staying on the dotted line DM, which is perpendicular to the concentration axis, and if at the same time we use up the other degree of freedom by moving along DM, that is by varying the temperature, our system is invariant. The third intensity factor, the pressure, will assume automatically a definite value (as

EO. At a point such as F, for instance, the *total* concentrations of silver and copper have *not* changed, but their concentrations in the solution phase *have* changed. Of the total concentration at F, there is an amount of silver proportional to FG, and an amount of solution proportional to FH. The concentration of the solution is represented by GI/GH. At point O we have four phases, vapor, solution, silver, and copper. Since $F = 4 - 4$, we have no degrees of freedom. This point is called the *entectic* point. The alloy which separates out on further cooling, and having the concentration represented by O is the *entectic alloy*. It must have, obviously, a definite melting point. At any point below JK we have a solid solution of one of the metals in the entectic.

Graphs such as these can be drawn for any system if we have the necessary data. Many of them have proven to be of great value from an industrial point of view, as can be seen from the illustration given. It is the hope of the writer that this short exposition will lead industrial chemists to study their "systems" from this point of view.

NEW USES FOR INFUSORIAL EARTH.

Infusorial earth is being mined more actively in California and Nevada, which produced nearly 90 per cent of the 6,582 tons output last year in the United States. The value, according to a recent daily consular and trade report, average \$10.50 per ton. Heretofore diatomaceous or infusorial earth has been largely used as an abrasive in the form of polishing powders and scouring soaps, but the United States Geological Survey finds that of late its uses have been considerably extended. Because of its porous nature it has been used in the manufacture of dynamite as a holder of nitroglycerine, but so far as known not in the United States. Its porosity also renders it a non-conductor of heat, and this quality in connection with its lightness has extended its use as an insulating packing material for safes, steam pipes, and boilers, and as a fireproof building material. In this country a new use of the material is reported in the manufacture of records for talking machines. For this purpose it is boiled with shellac, and the resulting product has the necessary hardness to give good results. In Europe, especially in Germany, infusorial earth has lately found extended application. It has been used in preparing artificial fertilizers, especially in the absorption of liquid manures; in the manufacture of water glass, of various cements, of glazing for tiles, of artificial stone, of ultramarine and various pigments; of aniline and alizarine colors; of paper, sealing wax, fireworks, gutta-percha objects, Swedish matches, solidified bromine, scouring powders, papier-mache, and many other articles. There is a large and steadily growing demand for it.

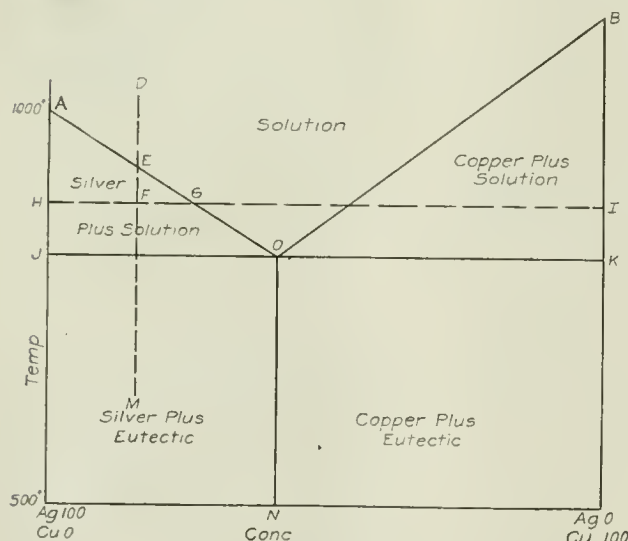


Fig. 2.

long as we keep the vapor phase) and we get the slope of the surface along DE. Of course, if we give up one of our phases (the vapor) we gain a new degree of freedom (along the p axis), for here

$F = 4 - 1$ instead of $F = 4 - 2$ as before.

As we touched E, the intersection of DM with OA, we have 3 phases: vapor, solution and solid silver. Our system of E is univariant for $F = 4 - 3$. If we choose to make the temperature our degree of freedom, the concentration changes automatically, following the line

RECENT VIEWS ON MATTER AND ENERGY.*

By DR. SAUL DUSHMAN.†

"The close of the old and the beginning of the new century has been marked by a very rapid increase of our knowledge of that most important but comparatively little known subject—the connection between electricity and matter. No study has been more fruitful in surprises to the investigator, both from the remarkable nature of the phenomena exhibited and from the laws controlling them. The more the subject is examined, the more complex must we suppose the constitution of matter in order to explain the remarkable effects observed. While the experimental results have led to the view that the constitution of the atom itself is very complex, at the same time they have confirmed the old theory of the discontinuous or atomic structure of matter. The study of the radio-active substances and of the discharge of electricity through gases has supplied very strong experimental evidence in support of the fundamental ideas of the existing atomic theory. It has also indicated that the atom itself is not the smallest unit of matter, but is a complicated structure made up of a number of smaller bodies."¹

Upon these atomic theories of electricity and matter there has been superposed in the last few years an atomic theory of energy which promises to alter radically all the ideas that have been held hitherto on the nature of energy and its mode of transmission. The experimental observations on the laws of distribution of radiant energy have led to conclusions that are apparently opposed to the electrodynamical equations deduced by Maxwell from the principle of least action. It has been shown that the view that energy is emitted and absorbed continuously is unable to explain the variation in distribution of radiant energy with the frequency of the radiation when this frequency is very high. An atomistic view of energy—or *quantum theory*, as it has been designated—is necessary not only in order to account for the observations of Lummer and Pringsheim and others on the distribution of intensity of radiation in the ultra-violet and visible portions of the spectrum, but this theory also leads to conclusions that are strikingly confirmed by observations in such vastly different fields of investigation as those of specific heats, the photo-electric effect and the production of X-rays.

And piling Pelion upon Ossa, the scientific iconoclast finally concludes that matter in itself has mass only in virtue of the motion of its constituent electrons, thus robbing us at once of what we had hitherto supposed to be a fundamental attribute of matter.

Never in the history of science has there existed such a period as the present: A period in which discoveries have multiplied more rapidly and the scien-

tific imagination has risen to higher flights. It is an epoch.

"When every morning brings a noble change,
And every change brings out a noble knight."

Within the past two decades we have seen the discovery of X-rays and radio-active phenomena on the one hand, and the evolution of the electron and quantum theories on the other. It has been found necessary to discard the old idea that the atoms of the elements are permanently stable and to replace this by the view that the atoms of the radio-active elements are "unstable dynamical systems," while it is quite probable that the atoms of all the elements are more or less unstable.

One of the first conclusions drawn from the application of the theory of energy quanta was that regarding the nature of X-rays. A large amount of experimental evidence has been obtained in the last two years confirming this conclusion and now we have every reason to believe that X-rays as well as gamma rays are electromagnetic waves of extremely short wave length, the frequency of these radiations being about ten thousand times as great as that of ordinary visible radiation.

Laue, the Braggs, and others have shown how X-rays may be utilized to *determine crystal structures*. Mosely and Darwin have still more recently investigated the X-ray and gamma ray spectra of a large number of elements and their observations are most easily interpreted in terms of the atomic model which had been previously suggested by Rutherford and Bohr. Not only are we learning something about the manner in which the atoms and molecules arrange themselves to form crystal structures, but we seem to be on the verge of learning something about the innermost structure of the atom itself.

This is not all. The very concept of matter itself is being questioned. We have been familiar for some time with the notion that the electron possesses mass in virtue of its charge. Now the work of Marsden and Geiger on the scattering of α -particles when passing through different substances led Rutherford to the suggestion that the mass of the positive nucleus itself may also be of electrical origin.

The most fundamental magnitude of physics and chemistry is therefore the unit negative charge or electron. Maybe there exists a positive electron corresponding to this unit of negative electricity and it is probable that the positive nucleus of the hydrogen atom is this long-sought-for unit of positive electricity. But the great outstanding fact is that all the investigations of recent years are converging towards a monistic view of natural phenomena. As mentioned above, we have atomic theories not only of matter and electricity but also of energy. Everywhere we are confronted with discontinuities in regions which have hitherto been assumed to be best represented by continuous functions.

*From General Electric Review.

†Research Laboratory, General Electric Company.

¹E. Rutherford, Radio-active Substances and Their Radiations, 1913, p. 1

The later conclusions must, however, be regarded as not being distinctly at variance with the older views but rather as an extension and evolution of the older theories which have been found necessary, owing to the accumulation of a large amount of new experimental evidence. We must never lose sight of this point, that the observations must always precede the theory and while the latter may be in a state of continuous flux, the facts remain. To evolve a unitary concept which shall reconcile the known facts of the past with the results of recent investigations is a stupendous undertaking; but the difficulties are by no means insurmountable and judging from the vigor with which the whole problem is being attacked by the foremost scientists of the present time, it is quite certain that the next decade will see developments in physics even more startling than have been accomplished in the past two decades.

As yet the effect of those altered views has been felt mainly by the theoretical physicist. To the practical physicist, the engineer at large, the chemist, and interested layman, these new concepts are either unfamiliar or else disregarded because of a much advocated doctrine which may be labeled empiricism, pragmatism, or agnosticism, according, as befits the philosophical views of each individual.

But just as the speculations of Carnot, Meyer and Clausius formed the foundation upon which the engineer of the present has developed methods of energy transformation, just as the almost incomprehensible flights of imagination of Maxwell were realized in the wireless waves as used commercially today, even so no doubt those atomistic theories of energy and electricity which we see under evolution at present will form the starting points for new developments by the engineer, whose happy function it has always been to realize in tangible form what the physicist beholds only as a vision.

It has been thought that an account of the results of the recent investigations might be of interest to that large class of readers whose daily labor is apt to get them out of touch with such developments. If, in the attempt to carry out this object, the writer shall have succeeded in imparting to his readers even a fraction of the information and inspiration that he has derived from the writing of the paper, he will deem his efforts amply rewarded.

ATOMIC THEORY OF ELECTRICITY.

Charge on a Univalent Ion in Electrolysis.—The ionic theory of solution has familiarized us with the idea that atoms or certain groups of atoms in solution carry electric charges which are integral multiples of that carried by a charged atom of hydrogen. These charged atoms or groups of atoms, known as ions, are the carriers of the electric current in the solution and liberate their charges at the electrodes during the process of electrolysis. Thus in the case

of a solution of hydrogen chloride (HCl), the ions are
 $\begin{array}{cc} + & - \\ \text{H} & \text{Cl} \end{array}$
 the positive and negative signs denoting that the hydrogen and chlorine ions are transported during electrolysis in the positive and negative directions of the current, respectively.

From Faraday's law and a knowledge of the number of atoms contained in one gram-ionic weight² of a substance it is possible to calculate the charge per atom, or the *unit electric charge*. According to Faraday's law, the electric charge carried by 1.008 grams of hydrogen (one gram-ion) is 96,540 coulombs. The number of atoms contained in the above weight of hydrogen is the same as the number of molecules per gram-molecular weight. This is usually denoted by N and according to the most accurate determination it has the value 6.06×10^{23} .

The unit electric charge as deduced from observations on conduction through electrolytes is therefore

$$\frac{96540}{6.06 \times 10^{23}} = 1.57 \times 10^{-19} \text{ coulombs.}$$

Since 1 coulomb is equal to 10^{-1} electromagnetic units (e.m.u.) or 3×10^9 electrostatic units (e.s.u.) the electric charge on a univalent ion in solution may be expressed as 1.57×10^{-20} e.m.u. or 4.78×10^{-10} e.s.u.

Furthermore, the ratio of the charge to the mass of a hydrogen atom in electrolysis (e/m) is 9.654×10^3 e.m.u. per gram.

Cathode Rays. Ratio of Charge of Mass.—In the case of the conduction of electricity through gases and metals, the same question arose as to the nature of the carriers of the electric charges. Obviously the conduction does not take place by means of charged atoms or groups of atoms as in the case of electrolytes. J. J. Thomson, continuing the experiments of Crookes on the nature of the electric discharge in high vacua, showed that the cathode rays observed in these experiments consist of *negatively charged corpuscles* which starting from the cathode move with very high velocities in straight lines and produce a vivid fluorescence wherever they strike the glass walls of the tube. Now it was shown a long time ago by Rowland that a charged particle in motion must produce the same effects as are observed in the case of a wire carrying current. In other words, the direction of motion of a charged particle will be affected by magnetic and electrostatic fields just as a wire carrying current. Furthermore the magnitude of the effects observed depends upon the ratio of the charge (e) to the mass (m) of the particles and upon their velocity. By observing the amount of deflection suffered by the cathode rays when subjected to magnetic and electrostatic fields, J. J. Thompson concluded that the negatively charged corpuscles constituting these

²The Gram-molecular weight of any substance is that weight in grams corresponding to its chemical formula. Similarly the gram-ionic weight is the weight in grams corresponding to the formula of the ion.

rays have a value of e/m of about the order of magnitude of 1.2×10^7 e.m.u. per gram. Later experiments have led to the more accurate value of 1.76×10^7 . The velocity of the corpuscles was found to vary from 10^7 to 10^9 cms. p.s.

Comparing the above values of e/m with that obtained for hydrogen ion in electrolytic conduction (9.64×10^3 e.m.u. per gram), the conclusion follows that either the unit electric charge is much greater in the latter case than in that of the cathode rays or that the mass of the negatively charged corpuscle is

$$\frac{9654}{1.76 \times 10^7} = \frac{1}{1835}$$

of that of the hydrogen atom.

Now, apart from the evidence obtained by a large number of experimenters that the corpuscles constituting the cathode ray beams must have masses much smaller than that of the hydrogen atom, there are definite reasons for believing that the unit electric charge in the cathode ray discharge has the same value as that possessed by the hydrogen ion in electrolytic conduction.

Unit Charge in Gaseous Conduction.—When X-rays pass through a gas they cause the latter to become conducting, that is ions are produced throughout the gas. These ions possess the property of acting as condensation nuclei for water-vapor in a supersaturated state and, by varying the conditions of the experiment, the condensation may be made to occur either on the positive or negative ions. By noting the rate of fall of the cloud formed by this condensation, measuring the total charge carried by the condensation produced and knowing the degree of supersaturation of the vapor, it is possible to determine the minimum charge carried by each ion, and consequently the unit negative charge concerned in gaseous conduction. This was the method adopted by C. T. R. Wilson in 1898.

Within the past two years Prof. Millikan has, however, obtained much more accurate data by the "oil-drop method." In this method the ions produced by the action of X-rays attach themselves to oil-drops suspended between two horizontal plates which are connected to the terminals of a high voltage battery, so that the rate of fall of the charged oil drops can be measured both in the absence of an electric field, and under the combined action of the latter and gravity. From observation on the rate of fall under these different conditions, it is possible to calculate the charge carried by the oil-drop. It was found by Prof. Millikan that in all his observations, the actual magnitude of this charge was always an integral multiple of that calculated for a hydrogen ion in electrolysis, viz.: 4.8×10^{-10} e. s. u.; furthermore that while the charge on any oil drop under observation altered from time to time owing to collision with other ions or molecules, the magnitude of the change was never less than 4.80×10^{-10} e. s. u. The most accurate value of this unit electric charge according to Prof. Millikan's most re-

cent determinations is $4.77 \pm 0.009 \times 10^{-10}$ e. s. u.

These investigations thus lead to the conclusion that the unit electric charge is the same for both gaseous and electrolytic condition. Consequently the mass of the negatively charged corpuscle constituting the cathode-rays must be $1/1835$ of that of the hydrogen atom.

Electron Emission from Hot Bodies. Photo-Electric Effect.—The cathode-rays of an ordinary discharge tube such as is used for the production of X-rays is not the only case in which these negatively charged corpuscles, or *electrons*, as they have been designated, are obtained in the free state. O. W. Richardson³ and his associates have shown that heated metals emit negatively charged corpuscles with the same value of e/m as that obtained for cathode rays. The number of these electrons emitted per unit area of surface increases rapidly with the temperature according to the formula

$$i = A \sqrt{T} e^{-\frac{b}{T}} \quad (1)$$

where A and b are constants and i denotes the current per unit area.

Dr. W. D. Coolidge⁴ has utilized this phenomenon in the construction of an X-ray tube in which the X-rays are produced by the bombardment of a tungsten anode by electrons moving with very high velocity. As source of electrons he used a heated tungsten filament.

In further elaboration of Richardson's work, Dr. I. Langmuir⁵ has shown that under certain conditions the electrons emitted from the heated metal can produce a space charge outside the metal which prevents the emission of more electrons and quantitative confirmation has been obtained by the writer⁶ of the conclusions deduced by him on the assumption that the thermionic currents obtained are due to the actual emission from heated cathode of charged particles having a ratio of charge to mass of the same value as that obtained for the electrons in cathode ray tubes.

Electrons are also emitted from all metals under the influence of ultra-violet light. This is the well-known photo-electric effect. The more electro-positive the metal, the lower the frequency of the light that is capable of causing photo-electron emission, and in the case of the alkali metals photo-electric currents of considerable magnitude are obtained even when ordinary light is used as a source of illumination.

In the case of both thermionic and photo-electric emission we are dealing with pure electron currents in a vacuum. There is an actual convection of negatively charged corpuscles from the heated metal or illuminated surface (which has to be charged negatively) to the anode. It is true that, within the past two or three years, doubt has arisen among a large number of investigators as to the existence of such pure electron

³Trans. Am. Electrochem. Soc. 22, 69 (1912).

⁴Phys. Rev., 2, 1913.

currents in high vacua. The tendency has been to ascribe both thermionic and photo-electric effect to chemical reactions occurring at the surface of the metal. But the results obtained by Dr. Langmuir and his associates on the thermionic currents in very high vacua and by Millikan, Richardson, the writer and others on the photo-electric effect in the best vacua obtainable, only seem to confirm the older views that such pure electron currents actually exist *per ipse* and are not due to any secondary effects due to the presence of gases.

Electron Theory of Conduction in Metals.—The emission of electrons from heated metals and under the influence of ultra-violet light can only be explained on the assumption that at any temperature there are present in the metal a certain number of free electrons and that there exists an equilibrium between the concentration of these free electrons inside the metal and in the surrounding space. With an increase in temperature the concentration of free electrons in the metal increases and consequently the emission of electrons also increases. The electrons must therefore be regarded as an essential constituent of all atoms.

According to the most recent theory, that suggested by Bohr, the atom is considered as being composed of one or more rings of electrons which are in constant rotation about a positively charged nucleus, the total charge on the latter being equal and opposite to that on all the electrons external to it. Owing to the vibrations among the atoms themselves, some of these electrons acquire sufficient kinetic energy to enable them to travel out beyond the influence of the forces which ordinarily hold them at a fixed distance from the positive nucleus. The latter is consequently able to attract any other free electron that comes within its field of attraction. At any instant there are thus present a certain number of free electrons, and it is by means of these free electrons that both electric charges and heat are conducted through the metal. An electron theory of conduction was suggested even before the investigation of J. J. Thompson by Riecke and Drude. The latter was able in this manner not only to give a theoretical basis to the well-known Wiedemann-Franz relation, according to which the ratio of thermal to electrical conductivity at any temperature is approximately the same for all metals, but he showed that there exists an intimate relation between the electrical conductivity and the thermo-electric properties of any metal.

Regarding the actual number of free electrons present under given conditions, we are as yet unable to draw any definite conclusions. The electron theory of conduction is as yet in a far from completed state. Recent speculations⁷ of Keesom and others indicate that a theory in harmony with all known observations will probably be developed in the very near future. But even in its present state the theory proves of consid-

erable advantage correlating a large number of phenomena while simplifying a number of concepts that are prevalent in electrical engineering.

Considering an electric current in a metallic conductor as due to a convection of charged particles, it is seen that electrical resistance may be simply regarded as a frictional resistance tending to oppose the flow of current. It follows also that the energy which we ordinarily conceive as being used to establish a magnetic field is really the energy required to set the electrons in motion, in other words, to overcome the inertia of the charged corpuscles. The same amount of energy must be restored to the conductor when the stream of electrons is suddenly stopped. The physical significance of what is meant by inductance thus becomes apparent.

Again, if the electron is made to oscillate backwards and forwards, as in the case of an alternating electric current, the magnetic field at any point in space must vary correspondingly and since the electron also exerts an electrostatic force, the magnitude of this at any point in space must also vary in a similar manner. In other words, if the motion of the electrons in the wire is harmonic, there will be propagated into the surrounding space two linear harmonic disturbances at right angles to each other and to the direction of motion of the electron. One of these disturbances will cause variations in the magnetic intensity at any point in space, while the other will cause corresponding variations in electro-static force. It is also evident that such disturbances will affect the electrons in other conductors and these electrons will consequently execute harmonic vibrations of the same frequency as that of the original exciting electrons. That is, an electromagnetic wave is produced.

Zeeman Effect. Explanation in Terms of Electron Theory.—The explanation of the Zeeman effect in terms of the electron theory must be regarded as one of the most important triumphs of this theory.

Assuming in accordance with Bohr's theory of the structure of the atom that light is produced by the vibration of electrons in the atom around a positive nucleus, it easily follows that the frequency of this vibration ought to be affected by a magnetic field, for the latter will exert a force which will either aid or oppose the centripetal force which is exerted by the positive nucleus on the rotating electron, according as the direction of rotation is either right-handed or left-handed with respect to the lines of magnetic force.

If now a source of monochromatic light emitting radiation of frequency γ_0 is placed in a magnetic field, the frequency of some of the electrons is increased while that of others is decreased. The consequence is that instead of one line in the spectrum we perceive three lines, the two outer ones being due to the vibrations set up by the electrons whose orbits are affected in opposite senses, while the center line has the same

⁶Phys. Rev. 2, 450 (1913).

⁷Phys. Rev., 3, 65 (1914).

⁷Phys. Zeitschrift, 14, 665 (1913).

frequency as the original light and is due to the electrons whose orbits are situated in a plane that is parallel to the direction of the lines of magnetic force.

Denoting the frequencies corresponding to the outer lines by γ^1 and γ respectively, it was shown by Lorentz that

$$(\gamma^1 - \gamma) \frac{2\eta c^2}{H} = \frac{e}{m} \quad (2)$$

Here c denotes the velocity of light and H the strength of the magnetic field. The values of e/m deduced by this method have been found to be in good accord with those obtained by measurements on cathode rays and are recognized as of equal weight with these other values.⁸

A similar explanation has been given of the observed rotation of the plane of polarization by a substance in a magnetic field (Faraday effect).

Electron Theory of Magnetism.—The electron theory of magnetism is one of the most important and most interesting applications of the new views. It is evident that the rotation of an electron about its nucleus must produce a molecular magnet having its axis perpendicular to the plane of rotation of the electron. This is the fundamental idea of the electron theory of magnetism. Langevin and Weiss have extended the theory to explain the phenomena of para- and ferro-magnetism. To explain the latter, Weiss has introduced the idea of magnetons or elements of magnetic moment corresponding to electrons.⁹

Summary.—The above are only a few of the many fields of application of the electron theory. It has proven of immense value in correlating a large number of observations, which is after all the prime purpose of any theory, and furthermore its application has led to the discovery of a large number of new phenomena which would not have been otherwise suspected.

Let us review then very briefly what we have learnt regarding the evidence upon which the theory is based and its main assumptions. The fundamental experiments upon which it is based are those of J. J. Thomson and others, showing that electrical conduction in gases takes place largely by means of small negatively charged corpuscles having a ratio of charge to mass which is 1835 times as great as that for hydrogen in electrolysis. Another line of investigation has led to the conclusion that the unit negative charge is the same in all cases. Consequently the mass of the negatively charged corpuscles or electron must be $1/1835$ of that of the hydrogen atom.

In other words, we are led to the conclusion that electricity is transported in multiples of a unit charge which has the magnitude of 4.8×10^{-10} e. s. u. This may therefore be said to be an atomic theory of electricity, similar to the older atomic theory of matter.

The electron theory of the constitution of the atom gives a logical explanation of all the phenomena of conduction. According to this theory the atoms of all elements contain under normal conditions one or more negatively charged corpuscles together with a positive nucleus.

Under the influence of different re-agents, such as ultra-violet light, high temperature, X-rays, γ -rays, or an intense electric field, the atom may lose one or more of its electrons, and the latter are then emitted with velocities that vary from 10^7 to 10^9 cms. per second. These electrons travelling with high velocity are capable of detaching more electrons from gas molecules with which they collide and thus produce the phenomenon of ionization by collision. The positively charged residues or ions produced in this manner are attracted to the cathode of the discharge tube and bombard it with velocities sufficiently great to cause the emission of more electrons. We thus obtain the various phenomena of gaseous conduction which vary from the Geissler discharge to the arc.

Again the drift of these electrons in metallic conductors under the influence of the electric force constitutes a current, and for the quantitative explanation of this phenomenon, it is only necessary to assume that, owing to the vibrations of the atoms in the solid, there is a continual separation of electrons from these atoms as well as a re-combination of the free electrons with the charged residues so that there is always present a small number of free electrons. On this assumption it is then possible to represent physically not only such electrical concepts as resistance and inductance, but also the mechanism by which electro-magnetic radiations are emitted and absorbed.

The electron theory of conduction enables us not only to deduce the relation between electrical and thermal conductivity of metals, (Wiedemann-Franz law) but also indicates relations between the electrical conductivity and thermo-electric properties.

Finally, the theory has also received splendid confirmation in the explanation of the Zeeman effect and other magneto-optical phenomena.

References.—For those who are interested in obtaining more explicit information on the subject the following references may be of interest.

1. *Fournier D'Albe. The Electron Theory*, 1906. Non-mathematical and popular exposition.
2. *E. P. Adams. Radio-activity*. A series of five lectures delivered before the American Institute of Electrical Engineers, New York, March and April, 1913. (Proc. Vol. 32, pp. 1159-1233). The last two lectures deal especially with the electron theory and contain an excellent summary of the fundamental points. No difficult mathematics.
3. *N. Campbell. Modern Electrical Theory*, 1913. The best work in English on the whole field of recent physical developments. Mathematical in parts.

⁸Kaye and Laby, *Physical Chemical Constants*, pp. 99.

⁹E. H. Williams, *The Electron Theory of Magnetism*. Bull. 63, Univ. Illinois Engineering Experiment Station.

METALLURGY.

THE HYDRO-ELECTROLYTIC TREATMENT OF COPPER ORES.*

By ROBERT RHEA GOODRICH.

It is the intention of this paper to give a brief summary of the practised and suggested hydro-metallurgical processes for the extraction of copper from its ores. The review of the literature as given contains the salient points of what has been done in the history of the subject.

The problems of economically treating low-grade copper ores have turned the attention of metallurgists toward such hydro-metallurgical problems as are encountered with low-grade siliceous, oxidized and sulphide ores, and concentrates, especially where water-power is cheap and fuel is expensive. The treatment of tailings from concentrates is another promising field for leaching methods, there being no other known possible method for economically extracting their copper contents. The same is also true of complex refractory ores which are not amenable to smelting for the recovery of their several metals. And, lastly, there are metallurgists who entertain hopes of discovering a leaching method which will radically change all methods of copper extraction to something quicker and cheaper than the present smelting methods.

CLASSIFICATION OF HYDROMETALLURGICAL PROCESSES.

I. PURELY CHEMICAL METHODS:

1. Alkali processes.
2. Sulphite processes.
3. Sulphate processes.
4. Chloride processes.

Copper is dissolved and precipitated by chemical reagents.

II. ELECTROLYTIC METHODS:

1. Sulphate processes.
2. Chloride processes.

Copper is dissolved chemically and is precipitated electrolytically. The deposition is usually accompanied by regeneration of the solvent.

All acids react more or less with the constituents of the ore, causing:

- a. Consumption of acid.
- b. The bringing in of elements detrimental to the process.

Iron, arsenic, antimony and bismuth, while detrimental, are not necessarily fatal to an acid process. If lime, magnesia, zinc or manganese occur in large quantities in the ore, acid processes are not applicable—the limit can only be determined by experiment. While calcium carbonate is detrimental, calcium

sulphate is not. Alumina is undesirable, but not necessarily very injurious.

Many oxidized ores are improved by roasting.

All sulphide ores require roasting for most of the leaching processes, the exception being chalcocite ores, which may be leached direct. (Greenawalt, "Hydro-metallurgy of Copper," 1912 Ed., Chap. IX.)

1. PURELY CHEMICAL METHODS.

1. Alkali Processes.

The alkali processes have not met with much encouragement in the hydrometallurgical extraction of copper from its ores, due largely to the low and slow solubility of copper minerals in solutions of the alkalis. Ammonia and ammonium compounds are the only alkaline solvents tried for the leaching of copper oxide ores on a commercial scale. (Greenawalt, p. 172.)

The Mosher-Ludlow Ammonia-cyanide Process.—This process is applicable to ores containing oxide and carbonate of copper. At the ordinary temperature, ammonia (NH_3) forms a stable compound $[\text{Cu}(\text{NH}_3)_2]$ which readily dissolves in water containing slight excess of ammonia. At the boiling point of the solution the compound is broken up, hydrated copper oxide being precipitated. The distilled ammonia may be condensed and used for further treatment of the ore. When the ore contains gold and silver as well as copper, a weak solution of potassium cyanide is used to extract the precious metals subsequently to the copper. The gold and silver are precipitated by zinc. (Electrochemical and Metallurgical Industry, Mar., 1908, p. 128; Greenawalt, p. 172.)

2. Sulphite Processes.

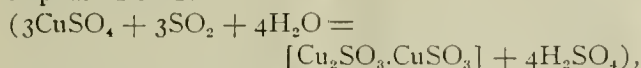
The Neill process is applicable to ores containing oxide and carbonate of copper. When cupric oxide is treated with water through which sulphur dioxide is passed, the following reaction takes place:



The cupric sulphite formed is insoluble in water, but is readily soluble in water containing an excess of sulphur dioxide. This constitutes the leaching step. Then the clear liquid is drawn from the ore and heated to drive off the excess sulphur dioxide, when a bright red, heavy precipitate $[\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3]$ is thrown down. Next, the liquid is run over iron to precipitate any copper that may remain in solution as sulphate. The liquid which contains no copper finally goes to waste. The experimental plant of the Montana Ore Purchasing Co., at Butte, was put up by Neill. Washing was difficult on account of ferric oxide which formed in the leaching charge. The results were: Ore, 3.15 per cent Cu; tailings, 0.31 per cent Cu; extraction, 90 per cent. (Greenawalt, p. 178.)

*From a paper presented at the 25th General Meeting of the American Electrochemical Society, in New York City, April 16-18, 1914.

The Van Arsdale process consists in precipitating the copper from cupric sulphate solution by adding sulphur dioxide



and heating with or without pressure

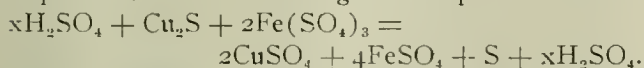


$\text{Cu} + 2\text{CuSO}_4 + 2\text{H}_2\text{SO}_4 + 2\text{SO}_2 + 2\text{H}_2\text{O}$), thereby simultaneously regenerating acid solution for leaching the ore. The regenerated sulphuric acid is double the amount required to dissolve the amount of copper precipitated. Only a part of the copper is precipitated. The process being cyclic, there is no particular harm in returning to the ore a solution containing a considerable amount of unprecipitated copper sulphate. (E. and M. J., June, 1908; U. S. Patent, Mar. 31, 1903, No. 723,949; Greenawalt, p. 179.)

3. Sulphate Processes.

Oxidized ores containing copper as oxide or carbonate may be treated directly with dilute sulphuric acid solutions. Sulphide ores, with the possible exception of certain chalcocite ores, should be roasted prior to leaching. The copper may be dissolved as sulphate either by (1) sulphuric acid or (2) metal sulphates. Reactions during leaching with sulphuric acid are: $\text{CuO} + \text{H}_2\text{SO}_4 = \text{CuSO}_4 + \text{H}_2\text{O}$, and during precipitation: $\text{CuSO}_4 + \text{Fe} = \text{Cu} + \text{FeSO}_4$. Theoretically, 1.68 lb. 66° B. sulphuric acid and 0.88 lb. iron are required to produce 1 lb. of copper.

Copper has been dissolved from its ores by ferric sulphate solutions containing free sulphuric acid:



Cuprous sulphide is slowly acted upon by solution of ferric sulphate. Most of the improvements of this simple process are based on the regeneration of the solvent. (Greenawalt, p. 180.)

Sulphuric Acid Leaching of Oxidized Copper Ores at Clifton, Ariz.—The Arizona Copper Co. has been leaching oxidized surface ores at Clifton on a large scale since 1893.

The sulphuric acid is manufactured from roaster gases. The Joy Mine, Morenci, furnishes the pyrite ore, containing 1.5 per cent copper, which is crushed to 2-inch. The fines are roasted in a Herreshoff five-deck furnace. The coarse material goes to lump burners. The cinder from the roasting furnaces is smelted in blast furnaces. The resulting acid (chamber acid) is 52° B.

The ore which contains 2.5 per cent of copper is conveyed from the mines at Metcalf to the "Oxide Mill" at Clifton. The copper exists chiefly as malachite, together with some sulphides. By wet concentration, 25 per cent of the copper is extracted as concentrates, carrying 7 to 10 per cent of copper, which are smelted. Slimes carrying 2.4 per cent of copper go to the slime pond for settling; they contain too much soluble alumina to leach. The tailings, size 1 inch

to sand—75 per cent of them larger than 1/8 inch—go to the leaching vats. Circular wooden vats, with perforated false bottom for filter, are used for leaching. The solution is circulated by centrifugal pumps, one being supplied to each tank. Successive solutions are applied. The first solution to fresh ore (concentrator tailings) is one high in copper and low in acid. This solution, leaving the vat with practically no free acid, passes on to the precipitation tanks. There is then applied to the ore a solution containing more free acid and less copper, followed by a fresh acid solution and lastly a water wash. The copper contents of the liquors is precipitated on scrap iron. There being no free sulphuric acid, the consumption of iron is a minimum. Liquors free from copper are run to waste in earthen reservoirs and sink in the ground, thereby preventing contamination of the streams. There are consumed 2.6 lb. of 52° B. acid (1.82 lb. 66° B. Com.) per pound of copper extracted. No general rule can be given for strength of acid. The more soluble the gangue, the weaker should be the acid. The ore carries a trace of gold, which apparently is lost. (Greenawalt, p. 183.)

Leaching Plant at the Snowstorm Mine.—The vein at Larson, Ida., is a replacement in quartzite. Only the oxidized ore of the upper workings (consisting of cuprite, malachite and chrysocolla) is treated. The copper content is 3 per cent, with small gold and silver values. The process is: Crush the ore and treat in agitators with bleaching powder and sulphuric acid, thus converting the copper, gold and silver into chlorides. Separate the liquor, and precipitate the copper and gold on scrap iron. Treat the residue with hyposulphite of soda to dissolve the silver chloride, which subsequently precipitate by sodium sulphide. The saving is 90 per cent of assay value of the ore. (Greenawalt, p. 187.)

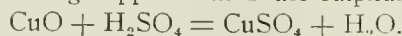
Copper Leaching Plant at the Gumeshevsky Mine, Russia.—The mine was shut down in 1871. The mine owners contracted with an old acid manufacturer to manufacture acid on the property from pyrite carrying 3.5 to 8 per cent of copper; to sell 53° B. acid to them at \$4.32 per ton; to extract the copper from the burned pyrite, leaving less than 0.3 per cent of copper in the tailings; to pay the owners \$145 to \$175 per ton of copper produced. The method used to extract the copper from the burned pyrite was: Roast burned pyrite with addition of sulphuric acid in a muffle furnace at 450° C. to 550° C., bringing copper into soluble condition; leach with water; leach with barren solution after precipitating on cast iron plates; leach with dilute sulphuric acid; precipitate copper at boiling temperature on cast iron plates. Consumption of acid, 2 lb. (66° B. Com.), and of cast iron, 1 to 2 lb. per pound of copper produced.

The mine owners worked the extensive dump left from the earlier working of the mine, when it was worked for oxidized ore only. The process was: Crush dump material by rock breaker and Chilean mills; leach with dilute sulphuric acid; precipitate

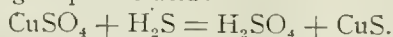
copper by cast iron, granulated or in plates. The oxidized dump material treated contained 0.75 per cent copper; of this 0.43 per cent was recovered, the balance going into the tailings. Extraction, 57 per cent. Insoluble copper existed as silicate and native copper. Consumption of acid, 7.4 lb., and of iron, 1.9 lb. for 1 lb. of copper produced. Thus only 23 per cent of acid consumed was usefully employed in dissolving copper; the balance acted on worthless gangue. All tanks, both for leaching and for precipitating, were rectangular and made of concrete. The agitator moved longitudinally in the leaching tank. (Greenawalt, p. 187; Inst. of Min. and Met. Bull., No. 65; Trans. I. M. M., XIX, p. 212; Min. Ind., 1910, p. 210.)

The Laist Process.—The process is based on the use of sulphuric acid as the solvent and hydrogen sulphide as the precipitant. The steps in the process are as follows:

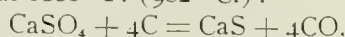
1. Dissolving copper with dilute sulphuric acid:



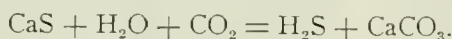
2. Precipitating copper by hydrogen sulphide and regenerating sulphuric acid:



3. (a) Manufacturing hydrogen sulphide by reducing calcium sulphate (gypsum) with coal, which takes place at 1800° F. (982° C.):



- (b) Decomposing calcium sulphide by carbon dioxide and water to hydrogen sulphide and calcium carbonate:



4. Converting copper sulphide precipitate to metallic copper by roasting and reducing in furnaces. In practice there was used for reaction 3 (a) about 2 $\frac{3}{4}$ lb. gypsum and 1 $\frac{1}{4}$ lb. of coal, which is but slightly above the theoretical amount. (Greenawalt, p. 204.)

Roasting and Leaching Tailings at Anaconda, Mont.—During the summer of 1912 experiments were made on regular concentrator tailings by roasting and leaching. The results were so satisfactory that it was decided to continue the work on a larger scale. In February, 1913, construction was begun on an 80-ton roasting and leaching plant. It was decided to precipitate copper by scrap iron and to experiment with precipitation by electrolysis and by hydrogen sulphide.

The roasting experiment was conducted in a regular No. 64 improved McDougal furnace. Two fire boxes were placed so that the flame could enter the third or the fourth floor (from the top). The third floor was selected as the better. The best results were obtained by oxy-chloride roasting. The firing was regulated by a pyrometer inserted on the fourth floor. The temperature was held at 1000° F. (538° C.). On the upper three hearths the ore was partly roasted. One per cent by weight of sodium chloride was added on the fourth floor.

The leaching was by percolation: No. 1 solution contained 3.5 per cent of H_2SO_4 and 10 per cent of

NaCl ; No. 2 solution contained 6 per cent of H_2SO_4 and 10 per cent of NaCl . Then followed water washes. The precipitation was done by hydrogen sulphide. No. 1 solution was the only one precipitated. No. 2 solution became No. 1 solution on the next vat. The acid strength was brought up in the precipitating vat. It was not necessary to add salt (NaCl), as the solution picked it up from the roasted ore.

Summary of Two Months' Operation.—In calcines to leaching plant: 10.4 lb. copper per ton, 0.46 oz. silver per ton.

Percentage of recoverable copper, 85.4 per cent; percentage of recoverable silver, 91.1 per cent.

Conclusions.—It is not advisable to leach high-grade 3 per cent copper material, which may be concentrated.

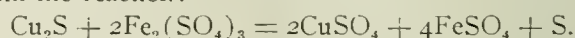
Material should be crushed to 15-mesh preparatory to roasting and leaching.

Copper set free by crushing should be taken out as high-grade concentrate and smelted.

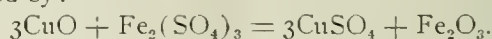
Sulphuric acid can be cheaply made at a smelting plant.

It is estimated that copper can be produced for 6.5 cents per pound. This is possible because tailings are already mined, crushed and sized; cheap acid may be made from roaster gases; operations are on a large scale. (M. and E. W., Vol. 39, No. 13, p. 545, Sept. 27, 1913; No. 14, p. 599, Oct. 4, 1913; Frederick Laist.)

Experiments with Ferric Sulphate at Cananea.—The dissolving of cuprous sulphide from the ores, by means of ferric sulphate solution, is in accordance with the reaction:



Thus, for 1 lb. of copper going into solution, 6.3 lb. of anhydrous ferric sulphate is consumed. Copper oxide is dissolved by ferric sulphate solutions, as expressed by:

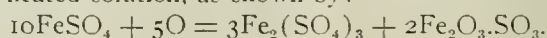


Thus in dissolving copper oxide, 2.1 lb. anhydrous ferric sulphate is consumed for 1 lb. copper going into solution.

At Cananea the consumption was found to be 4.37 lb. ferric sulphate per pound of copper extracted. The content of solution in ferric sulphate was of small import, provided basic iron salts were absent from it. The solution worked with as small an amount as 1 per cent. The extraction with a 2 per cent solution was nearly as complete as with a 7 per cent solution. From leaching, the liquor went to the precipitation tank, in which iron was used for precipitating the copper according to:



While the theoretical consumption of iron is 0.88 lb. for 1 lb. copper precipitated, the actual consumption was 1.5 times this amount. The solution was regenerated for further leaching by blowing hot air through the heated solution, as shown by:



Thus with a neutral solution, 40 per cent of the iron

content is precipitated as a basic salt ($2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3$). To prevent the formation of basic salt during the regeneration in the oxidizer, sulphuric acid must be supplied in an amount as indicated by: $2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + \text{O} = \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$. Since acid must be replenished, the process becomes virtually one of leaching with acid. In treating mill tailings, 65 per cent of the copper was extracted in 3 hours (liquor boiled). In treating a 10-ton lot of Cobre Grande ore containing 3 per cent of copper, extraction was 96 per cent. The cost per pound of copper was 6.4 cents. There was much trouble with the oxidizer in the regeneration of the spent liquor. (Greenawalt, p. 194; *Mines and Methods*, Sept., 1910, W. L. Austin).

Thomas' Experiments with Ferric Sulphate on Sulphide Ore.—The results were: Double sulphides of copper, which occur in nature, require for complete transformation by ferric sulphate, long treatment with fine crushing. The commercial application does not pay. Free copper sulphides and oxides react easily with ferric sulphate in aqueous solution. Double sulphides of copper (such as chalcopyrite) must be roasted. Roast at low temperature (sulphatizing), 450°C . to 480°C ., to produce the maximum amount of copper sulphate. The copper may then be leached with but small amount of ferric sulphate. (Greenawalt, p. 201; *Metallurgie*, Jan. 15, Feb. 8, 22, 1904).

Methods of Extracting Copper at Rio Tinto, Spain.—The ore is massive pyrite containing 3 per cent of copper, mostly as cuprous sulphide. The method in use at the present time is weathering, or aid-oxidation. The reactions are: $\text{Fe}_2\text{S} + 7\text{O} + \text{H}_2\text{O} = \text{FeSO}_4 + \text{H}_2\text{SO}_4$. Ferrous sulphate readily oxidizes, forming ferric sulphate: $2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + \text{O} = \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$. Half the copper goes in solution in a few months, reducing an equivalent of ferric sulphate: $\text{Fe}_2(\text{SO}_4)_3 + \text{Cu}_2\text{S} = \text{CuSO}_4 + 2\text{FeSO}_4 + \text{CuS}$. The following reaction is slow, taking two years to extract 80 per cent of the remaining half: $\text{Fe}_2(\text{SO}_4)_3 + \text{CuS} + 3\text{O} + \text{H}_2\text{O} = \text{CuSO}_4 + 2\text{FeSO}_4 + \text{H}_2\text{SO}_4$. The process is: Ore is piled in heaps containing 100,000 tons, with flues of rough stone at the base connecting with chimneys. The oxidation goes on rapidly. The temperature rises, but is not allowed to go above 170°F . (77°C .) at chimneys, otherwise the heap might catch fire. The regulating of the temperature is accomplished by closing the tops of chimneys. Water is run on top of the heap, leaching the copper. The outflowing copper solution, before going to the precipitation tanks, is sent to the filter bed of fresh ore, thus reducing any contained ferric sulphate and insuring minimum consumption of iron: $7\text{Fe}_2(\text{SO}_4)_3 + \text{FeS}_2 + 8\text{H}_2\text{O} = 15\text{FeSO}_4 + 8\text{H}_2\text{SO}_4$. After a year or two the copper contents is reduced to 0.3 per cent, corresponding to 90 per cent extraction. The ore is disposed of as "washed sulphur ore" (containing 49.5 per cent S), which is used for the manufacture of sulphuric acid; 99.5 per cent of the copper in the liquor is precipitated with a consumption of 1.4 lb. pig iron

(92 per cent Fe) per pound of copper recovered. (Greenawalt, p. 205; *T. A. I. M. E.*, Vol. XXXV, 1905, C. H. Jones).

Leaching Shannon Copper Ores.—Experiments were made by Francis S. Schimerka to find a practical leaching system for treating low-grade ore and tailings. The basic character of the ore makes sulphuric acid leaching impossible on account of the high acid consumption. Treatment with roasting gases gave successful results. The ore contained 1.9 per cent of copper, 0.55 per cent of sulphur and a minute trace of gold and silver. The direct leaching with sulphuric acid gave an extraction of 81 per cent, with acid consumption of 8.8 lb. per pound of copper extracted. The process employed was: The ore was subjected in heaps to roasting gases. At the base of the heap were constructed flues connecting with chimney for firing. At the bottom was placed a layer of 100 tons of pyrite containing 50 per cent of sulphur; then 1,000 tons of oxide ore, crushed to 2 inch, was placed on top, and finally covered with a layer of fines a foot thick. The heap was sprinkled with waste solution from the scrap-iron precipitation tanks, producing ferric sulphate according to: $2\text{FeSO}_4 + \text{SO}_2 + \text{O}_2 = \text{Fe}_2(\text{SO}_4)_3$. The roasted ore was leached with water in tanks with filter bottoms. The ferric sulphate formed by roasting dissolves copper which may not be water soluble. The outflowing copper solution, still containing some ferric sulphate, was run over tailings to reduce the last of the ferric sulphate before going to scrap-iron for precipitation of the copper. Extraction, 72 to 82 per cent. The advantages of this process are: (1) Coarse crushing; (2) cheap installation; (3) no sulphuric acid used; (4) commercial use of ferric sulphate solution, produced in excess of requirements.

Laboratory experiments by Francis S. Schimerka, on the treatment of ore and tailings, were conducted by roasting these materials in a muffle furnace and treating, as follows:

1. Ore containing 2.37 per cent Cu, 3.02 per cent S, was roasted at 535°C . Leached with 5 per cent H_2SO_4 solution. Extraction, 86.4 per cent. Consumption of acid, 3.19 lb. per pound of copper extracted—permissible in commercial practice.
2. Ore containing 2.01 per cent Cu, 2.58 per cent S. Ferrous sulphate was added in such amount that iron (Fe) was 2.8 per cent the weight of ore. Leached with 10 per cent H_2SO_4 solution. Extraction, 82.5 per cent. Consumption of acid, 1.2 lb. for 1 pound copper extracted.
3. Tailings, product of concentration of sulphide ores (basic in character), containing 0.83 per cent Cu, 0.88 per cent S, were roasted with addition of pyrite in largest amount permissible for profitable working. When using sulphuric acid for the leaching the lowest consumption was 7.41 lb. acid per pound of copper extracted. Extraction 60 per cent.
4. Tailings, treated like sulphide ores. Ferrous sulphate added in such amount that iron (Fe) was 1.4

per cent weight of ore. Roasted at 480° C. Ferric sulphate in roasted ore was 1.01 per cent. Water was added in amount equal to the weight of ore. Digested twelve hours with cold solution. Extraction 71.7 per cent. (E. and M. J., Vol. 96, No. 24, Dec. 13, 1913, p. 1107).

4. CHLORIDE PROCESSES.

The chloride processes have been widely applied. Hydrochloric acid presents certain advantages over sulphuric acid in technical application. Hydrochloric acid is less apt to form basic salts, and therefore yields solutions that contain but little free acid and which constantly require less iron for the precipitation of copper. Hydrochloric acid is usually more expensive than sulphuric acid. Ordinarily only oxidized ores are suitable to treatment by a chloride process. The copper may be dissolved by hydrochloric acid, or by a metal chloride. The reaction which occurs is: $\text{CuO} + 2\text{HCl} = \text{CuCl}_2 + \text{H}_2\text{O}$. (1.15 lb. HCl per pound Cu). The precipitation of the copper is expressed by: $\text{CuCl}_2 + \text{Fe} = \text{FeCl}_2 + \text{Cu}$. (0.88 lb. Fe per pound Cu). Theoretically, the same amount of iron is required for the precipitation as for precipitation of copper from sulphate solutions. Practically, sulphate solutions consume more iron than chloride solutions. (Greenawalt, p. 216).

In Stadtberg, Westphalia, hydrochloric acid was formerly used to extract copper from ores containing 1 to 2 per cent of copper. The process replaced a sulphuric acid process previously employed, but was abandoned when carbonates of the ore changed to sulphides in depth. The ore was leached in rectangular wooden tanks containing 90 tons. The fresh ore was treated with partially saturated solution until saturation took place. Ore nearly copper-free was treated with fresh 12.5° B. acid, and lastly with water wash. Acid consumption, slightly above the theoretical. (Schnabel, "Handbook of Metallurgy," Vol. I, p. 200; Greenawalt, p. 217).

Ferric chloride, like ferric sulphate, dissolves copper from ores containing the metal as oxide, carbonate and sulphide. (Cu_2S is the only sulphide easily soluble). The reactions are: $\text{Cu}_2\text{S} + 4\text{FeCl}_2 = 2\text{CuCl}_2 + 4\text{FeCl}_2 + \text{S}$, and $3\text{CuO} + 2\text{FeCl}_3 = 3\text{CuCl}_2 + \text{Fe}_2\text{O}_3$. The copper may be precipitated by iron: $\text{CuCl}_2 + \text{Fe} = \text{FeCl}_2 + \text{Cu}$. Regeneration of the ferric solution may be accomplished by means of air, causing one-third of the iron to precipitate: $6\text{FeCl}_2 + 3\text{O} = 4\text{FeCl}_3 + \text{Fe}_2\text{O}_3$. It may be regenerated by chlorine; produced chemically or electrolytically: $\text{FeCl}_2 + \text{Cl} = \text{FeCl}_3$. (Greenawalt, p. 218).

Doetsch Process.—This process was formerly applied to raw and to roasted ores at Rio Tinto, Spain.

1. Raw ores. The ore contained 2.7 per cent of copper. The pyrite was unaffected by leaching solutions. The process is: Crush to $\frac{1}{2}$ in. Mix with 0.5 per cent by weight of sodium chloride and 0.5 per cent of ferrous sulphate. Build in large heaps. Run on solution of ferric chloride. Precipitate copper on pig

iron. Regenerate solution in scrubbing towers by chlorine generated by roasting, according to: $2\text{FeSO}_4 + 4\text{NaCl} + 3\text{O} = \text{Fe}_2\text{O}_3 + 2\text{Na}_2\text{SO}_4 + 4\text{Cl}$. Extraction, 50 per cent in 4 months, 80 per cent in 2 years. Consumption of pig iron, 1.3 lb. per pound of copper produced. Cumenge estimates the cost as 3.3 cents per pound of copper.

2. Roasted ores. The ore of nut size is made into heaps of 800 tons, with 14 tons salt. Rough flues 20 inches square, used for firing, are constructed at the bottom and connected with chimneys. The reaction is shown by: $2\text{FeSO}_4 + 4\text{NaCl} + 3\text{O} = \text{Fe}_2\text{O}_3 + \text{Na}_2\text{SO}_4 + 4\text{Cl}$. The liberated chlorine produces ferric chloride and cupric chloride. Some of the roasted ore has been mixed at times with the unroasted ore for the extraction of the copper by the ferric chloride solution. (Greenawalt, p. 219; Annales des Mines, Vol. XCVI; Notes Sur le Rio Tinto, M. E. Cumenge).

The Froelich Process.—The ore is subjected, in the absence of air, to temperature between 150° C. and 800° C. Chlorine is introduced. After chlorinating, in order to regain the chlorine combined with the iron, heat to above 300° C., introducing a certain amount of air, when the ferric chloride is evaporated, and in the presence of air is decomposed into ferric oxide and chlorine. The cupric chloride is not changed by this treatment. Leach with water. Precipitate copper by iron. Oxidize ferrous chloride to ferric chloride in rotating drum by a blast of air. Drive off water of crystallization of ferric chloride. Heat to about 300° C. with a certain amount of air, thus regenerating chlorine for the process (Greenawalt, p. 223; U. S. Patent No. 846,657, March 12, 1907).

Ferrous Chloride Process.—Some years ago Hunt and Douglas based a process on the action of ferrous chloride on copper oxide and copper carbonate. Hunt says that chrysocolla ($\text{CuSiO}_3 + 2\text{H}_2\text{O}$) is likewise completely decomposed by a hot solution of ferrous chloride containing sodium chloride. The reaction given is: $3\text{CuO} + \text{FeCl}_2 = \text{CuCl}_2 + 2\text{CuCl} + \text{Fe}_2\text{O}_3$. The precipitation by metallic iron is said to be according to: $\text{CuCl}_2 + 2\text{CuCl} + 2\text{Fe} = 2\text{FeCl}_2 + 3\text{Cu}$. Cuprous chloride, which is insoluble in water, is soluble in solutions containing an excess of metal chlorides. Silver in ore is converted to silver chloride by cupric chloride, and is dissolved in solutions containing an excess of metallic chlorides. Theoretically, 0.59 lb. iron precipitates 1 lb. copper. An objection is that basic salts of iron clog the filter. Heat is not necessary, but it hastens the reaction. The silver will be precipitated with the copper. If it is desired to precipitate the silver separately, reduce all cupric chloride to the cuprous state by means of sulphur dioxide, then precipitate the silver on copper, and subsequently copper on iron.

The process, as formerly applied at Ore Knob, Ashe Co., N. C., is: Crush the ore to 40 mesh and roast to sulphate and oxide. Leach with hot solution of ferrous sulphate and sodium chloride (22° B.). Precipitate copper on iron, regenerating solvent: 0.7 lb. iron

precipitates 1 lb. of copper. Cost of the copper, 8 cents per pound. (Greenawalt, pp. 225-6; T. A. I. M. E., Vol. X, p. 12; T. A. I. M. E., Vol. II, p. 394, E. E. Olcott).

Hunt and Douglas Process.—This process is based on the following combination reaction: $2\text{CuSO}_4 + 2\text{NaCl} + \text{SO}_2 + 2\text{H}_2\text{O} = 2\text{CuCl} + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4$. The process is: Roast, if the ore is a sulphide, and extract the copper from the oxidized ore with dilute sulphuric acid regenerated in the process. Convert the cupric sulphate into cupric chloride by addition of a soluble chloride. Convert soluble cupric chloride into insoluble cuprous chloride by sulphur dioxide, with simultaneous regeneration of sulphuric acid. Convert the precipitated cuprous chloride into cuprous oxide, or metallic copper, by addition of milk of lime or replacement with iron. If the roasted ore contains silver, the sulphate of copper, which in well-roasted ore should be one-third of the content, is first leached out with water, care being taken to add just sufficient soluble chloride to render insoluble any silver present. From the clear solution thus obtained, after adding the requisite amount of sodium chloride to chloridize the copper, precipitate the copper by sulphur dioxide. The resulting liquor, freed from sulphur dioxide, is used to dissolve the oxide of copper in the ore. From the residues the silver may be extracted by brine, after which the gold may be recovered by chlorination. Chloride of silver is soluble to some extent in a solution of cupric chloride, and is then in part carried down with the cuprous chloride. (Greenawalt, p. 228; T. A. I. M. E., Vol. X and XVI).

Hunt and Douglas Process at Argentine, Kansas.—At the Kansas City Smelting and Refining Company's works the material treated was a lead-copper matte. In applying the process, using sodium chloride as chloridizer, sodium sulphate accumulated in the solution, which crystallized out, causing trouble. This trouble was corrected by using three parts of calcium chloride and one part of sodium chloride as chloridizers. Calcium sulphate formed, and, being insoluble, was precipitated. The necessary calcium chloride was produced in the process, in the conversion of cuprous chloride to cuprous oxide by milk of lime. The residue from the leaching went to the lead smelting department. (Greenawalt, p. 231; Mineral Industry, Vol. XVII, 1908, p. 296).

Modification of the Hunt and Douglas Process.—To simplify the operation, Hofmann worked out and successfully introduced the following modifications: Roast ore or matte as usual. Treat roasted ore or matte in agitating tanks with dilute sulphuric acid produced in the process: $\text{H}_2\text{SO}_4 + \text{CuO} = \text{CuSO}_4 + \text{H}_2\text{O}$. Chloridize with hydrochloric acid produced in the process, regenerating sulphuric acid: $\text{CuSO}_4 + 2\text{HCl} = \text{H}_2\text{SO}_4 + \text{CuCl}_2$. Convert the soluble cupric chloride into insoluble cuprous chloride by cement copper in an agitating tank. Heat by a steam jet, forming cuprous chloride: $\text{CuCl}_2 + \text{Cu} = 2\text{CuCl}$.

Treat the cuprous chloride in revolving barrels with a small amount of water, scrap iron and salt (sodium chloride). The salt helps to start the reaction by dissolving some cuprous chloride: $2\text{CuCl} + \text{Fe} = \text{FeCl}_2 + 2\text{Cu}$. Evaporate the ferrous chloride solution in an iron pan. Charge the solid ferrous chloride into retorts which are provided with water (or steam) and air, hydrochloric acid being regenerated for use in the process: $\text{FeCl}_2 + \text{O}_2 + \text{H}_2\text{O} = \text{Fe}_2\text{O}_3 + 2\text{HCl}$. This modified process was used for some time until Hofmann received instructions to change the plant over to the more profitable manufacture of blue vitriol. (Greenawalt, p. 241; Mineral Industry, Vol. XVII, 1908, p. 296, Ottokar Hofmann).

The Bradley Process.—The sulphide ore is carefully roasted at 450°C . to 550°C . in a roasting furnace known as the "amphidizer." The roasted ore is treated with calcium chloride solution in a reaction drum at 100°C ., converting copper sulphate into cupric chloride, and any ferric sulphate produced by roasting is changed to ferric chloride. The resulting calcium sulphate is insoluble. The ferric chloride which forms dissolves copper oxide, copper sulphide and metallic copper which may have remained unaffected by roasting. The gold and silver in the ore are brought into solution by adding free chlorine. The chlorides of silver and gold, soluble in calcium chloride solution, may be precipitated with the copper. After leaving the reaction drum the pulp is filtered. The solution is subjected to further oxidizing operations so as to be sure the metals are all combined at their highest valency. The solution is then in condition for treatment for the separation of the dissolved metals. (Greenawalt, p. 243; E. and M. J., Jan. 6, 1912; U. S. Patent, No. 1,011,562, Dec. 12, 1911).

Longmaid-Henderson Process.—This process consists in roasting pyrite cinder from sulphuric acid works with sodium chloride, leaching out the cupric chloride formed and precipitating the copper by iron. Longmaid obtained patents, Oct., 1842, and Jan., 1844, relating to the treatment of pyrite cinders by roasting with sodium chloride. He may be regarded as the pioneer in the field of the wet extraction of copper. Gossage, in 1850, first used sponge iron to precipitate copper. Henderson improved the process in 1865, adding absorption towers, so that the gases from chloridizing roasting yielded weak acid, which was used for leaching copper ores. The steps in the process are: Mix the roasted ore (pyrite cinder) with sodium chloride, and grind mixture. Chloridizing roasting. Leach the roasted ore. Precipitate the silver from the argentiferous liquors. Precipitate the copper from the desilverized liquor. Prepare the leached ore for the iron works. Analysis of average pyrite cinder, 4 to 5 per cent copper; sulphur, equal to or greater than copper. Mechanical furnaces use less salt than hand roasters, average 7.5 per cent.

In the German works at Oker, average results showed: 75 per cent of the copper soluble in water,

20 per cent of copper soluble in dilute hydrochloric acid, 5 per cent of the copper insoluble. The leaching of the roasted chloridized ore was done in wooden tanks with filter bottoms of perforated boards painted with coal tar. The process was: Weak liquor from previous tank was applied, going off as strong liquor to precipitation tanks. Then two hot washes were applied, producing weak liquor to be used again on another tank. Next, dilute tower acid was put on six times; a satisfactory extraction resulted. The acid liquors, which produce somewhat impure copper, may be precipitated separately. Copper precipitated from aqueous solution is pure. Copper precipitated from acid solution is impure. Most cupriferous pyrite contains some silver and small quantities of gold. Silver chloride soluble in other chlorides, and gold chloride soluble in water, are extracted with the copper. Formerly there were various schemes proposed for the separate recovery of gold and silver from copper. Now usually there is no attempt made to recover gold and silver separately from copper, because of the cheap electrolytic method of refining copper. The residue, "purple ore," was briquetted and sent to the blast furnace. (Greenawalt, p. 246; Lunge's Treatise on the Manufacture of Sulphuric Acid and Alkali, Vol. I, 1891).

The Longmaid-Henderson process as carried out at the works of the Pennsylvania Salt Manufacturing Company at Natrona, Pa., where 200 tons of pyrite cinder is treated per day, is: Grind to 20 mesh in Chilean mill with 10 per cent of salt. Add raw ore so that sulphur equals $1\frac{1}{2}$ times weight of copper. Charge 9,600 lb. mixture into the muffle roasting furnace, kept 8 hrs. at dull red heat, 800° C. Send roasted material to cooling floor, then to leaching vats. It is not desirable to precipitate silver by Claudet's iodide process, because it leaves 5 oz. silver to the ton of copper, and electrolytic refineries and blue vitriol works will pay for 95 per cent of the silver and all the gold and copper. Cost to treat one ton of pyritic cinder, \$1.87. (Greenawalt, p. 262; Mineral Industry, Vol. VIII, IX; Joel G. Clemer).

The cost of producing copper by the Longmaid-Henderson process in a modern plant, using mechanical roasters: Eastern U. S., treating per day 30 tons pyrite cinder containing 2.27 per cent Cu, 2.28 per cent S, was 5.2 cents per pound of copper. Western U. S., under similar conditions, it was 6.5 cents per pound of copper. (Greenawalt, p. 266).

Copper Precipitated by Chemical Reagents.—The copper precipitants used are: 1. Iron: Cast iron, wrought iron, sponge iron. 2. Hydrogen sulphide. 3. Lime.

1. Iron precipitates copper according to: $\text{CuSO}_4 + \text{Fe} = \text{Cu} + \text{FeSO}_4$; $\text{CuCl}_2 + \text{Fe} = \text{Cu} + \text{FeCl}_2$. (Theoretically, from solution of cupric salts, 0.88 lb. of Fe precipitates 1 lb. of Cu). $2\text{CuCl} + \text{Fe} = 2\text{Cu} + \text{FeCl}_2$. (From solutions of cuprous chloride, 0.44 lb. Fe precipitates 1 lb. Cl). Iron may be consumed by ferric salts and by free acid: $\text{Fe}_2(\text{SO}_4)_3 + \text{Fe} = 3\text{FeSO}_4$;

$2\text{FeCl}_3 + \text{Fe} = 3\text{FeCl}_2$; $\text{H}_2\text{SO}_4 + \text{Fe} = \text{FeSO}_4 + \text{H}_2$. Thus for minimum iron consumption the solution going to precipitation ("cementation") tanks should be free from ferric salts and low in acid.

At Stadtberg, Westphalia, where hydrochloric acid was used for leaching, 1.27 lb. iron precipitated 1 lb. copper. In the Hunt and Douglas process, 0.5 lb. to 0.7 lb. iron precipitated 1 lb. copper from cuprous chloride solutions. At Gumeskevsky Mine, Russia, where cast iron was used both in plates and granulated, it was found that tanks charged with 12 tons of granulated cast iron, placed in layers 4 inches thick on four inclined false bottoms gave as good precipitation as tanks charged with 115 tons of plates. Wrought iron scrap is much used.

It is often advantageous to make the iron on the spot. Sponge iron may be made by heating ferric oxide in a reducing atmosphere and cooling in a reducing atmosphere. In a measure it solves the problem of iron supply. It has long been known that iron sponge can be thus produced, but the idea has not met with much encouragement.

2. Hydrogen sulphide precipitates copper as cupric sulphide: $\text{CuSO}_4 + \text{H}_2\text{S} = \text{CuS} + \text{H}_2\text{SO}_4$; $\text{CuCl}_2 + \text{H}_2\text{S} = \text{CuS} + 2\text{HCl}$. Acid regenerated by the precipitation is returned to the ore to dissolve more copper. This does not regenerate all the acid applied to the ore; some acid must be supplied to the process.

3. Lime (calcium hydrate or milk of lime) is not suitable for precipitating copper from sulphate solutions on account of contaminating the precipitated copper with calcium sulphate. It was for a long time used with the Hunt and Douglas process, and was found to be a successful precipitant because the resulting calcium chloride is very soluble: $2\text{CuCl} + \text{Ca}(\text{OH})_2 = \text{Cu}_2\text{O} + \text{CaCl}_2 + \text{H}_2\text{O}$. (Greenawalt, p. 270 to 282; Lunge, "Sulphuric Acid and Alkali Manufacture," p. 815).

Regenerated sulphuric acid comes in an amount equivalent to the copper deposited. This acid will only partially supply the acid required for leaching ore, because a certain amount of acid is consumed by action on the gangue. Yet electrolytic precipitation is an advance over precipitation by metallic iron, in which case no acid is regenerated. Theoretically, 2.1429 lb. copper are deposited per kw. hour. This energy efficiency of 100 per cent cannot be attained, because it would require the ohmic resistance of the entire circuit to be *nil*. Fifty per cent energy efficiency may be expected. When using sulphur dioxide as depolarizer (see equation I [b]), where theoretical voltage equals—0.15 volt, no power will be required theoretically to deposit the copper, and the process will be placed on a par with electrolytic refining with a soluble anode. The practical power consumption depends upon the ohmic resistance of the circuit and the current density employed. Tosizza ascertained by experiment that by using sulphur dioxide as depolarizer the necessary impressed voltage

is diminished to 0.2 volt. Electrolytic refining uses 0.2 to 0.4 volt. (Greenawalt, p. 309; U. S. Patent 710,346, Sept. 30, 1902, Tossizza.)

Treatment of Ore by Braden Copper Co., Chile.—The plant consists of a modern concentrator, a smelter and a leaching plant capable of treating one-fifth of their output of concentrates. They estimated that on account of local conditions (cheap water power, etc.) the leaching of concentrates would be cheaper than smelting. The concentrates contain 16 per cent Cu, 19 per cent Fe and 22 per cent S. The process is: Roasting concentrates; manufacturing sulphuric acid for leaching; precipitating the copper electrolytically. (Greenawalt, p. 331; E. and M. J., Dec. 30, 1911, Pope Yeatman.)

The Chile Exploration Company, Chuquicamata.—The copper in this ore exists as brochantite ($\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$), which is insoluble in water, but soluble in dilute sulphuric acid. There is no arsenic, antimony or silver in the ore. The first 25 ft. of the ore body contains 0.02 per cent sodium chloride. A difficulty first met was that during electrolysis obnoxious chlorine gas was given off. The process developed by A. E. Cappelen Smith is: Crush to $\frac{1}{2}$ to $\frac{1}{4}$ inch. Leach in large open vats with dilute sulphuric acid. (Percolation, 16 ft. high.) Drain and wash with water. Run copper liquor, prior to electrolysis, over shot copper in order to eliminate the chlorine. The cuprous chloride thus precipitated is smelted at a low temperature with carbon and lime. Calcium chloride is slagged. There is no loss of copper by volatilization during smelting of the chloride. Deposit the copper electrolytically, using insoluble magnetic oxide anodes (Fe_3O_4). There is a gain of 5 kilos of sulphuric acid per ton of ore treated. Run 8 to 10 per cent of the liquor to waste. Extraction, 90 per cent. This is a leaching plant which is being operated under favorable conditions. The power is transmitted from the seacoast, 41 miles distant. (E. and M. J., Oct. 4, 1913, Vol. 96, No. 14, p. 651.)

The Butte-Duluth Mining Company, Butte, Montana.—The ore is a decomposed granite, containing 2 per cent of copper as malachite, azurite, chrysocolla and cuprite. The mining is by open cut method. The process is: Crush to $\frac{1}{2}$ inch. Send to leaching tanks. Leach with 10 per cent sulphuric acid solution, put on for 24 hours. Pass liquor through the temperature cells, where it is heated to 60° C. Send heated solution to electrolytic cells. Send electrolyzed lean solution to sump, where it is standardized to 10 per cent of H_2SO_4 . Return the replenished solution to leaching tanks. In washing, make first water wash small in quantity, and add to mill solution. Waste an equivalent amount of the mill solution, which, prior to wasting, is run over ore till neutral, and over scrap iron to precipitate the copper. With the six new electrolytic cells, output is 100 tons finished copper (96.96 per cent pure) per month. Acid consumption, 3.5 lb. per pound for copper. One pound copper per kw. hour. Cost, 13.7 cents per lb. copper. (Mining and

Eng. World, Sept. 6, 1913, Vol. 39, No. 10, p. 423, Copper Leaching at Butte, Montana, Peter E. Peterson.)

II. ELECTROLYTIC METHODS.

The successful electrolytic refining of blister copper has turned the attention of metallurgists to the application of similar operations in the extraction of copper direct from its ores. There are difficulties in the electrolytic extraction of copper from its ores that are not met with in the electrolytic refining of copper, yet these difficulties do not appear insurmountable.

In electrolytic refining a soluble anode is used. Theoretically, there is no consumption of energy, and no acid consumed or generated. With the soluble anode there is no serious difficulty. When copper is dissolved from the ore, conditions are different. The insoluble anode is the first serious difficulty. It is hard to find a good conducting substance which is not attacked during electrolysis. Graphitized carbon has given satisfaction with chloride electrolytes, but not with sulphate electrolytes. For sulphate solutions no satisfactory anode has been found; on the whole, peroxidized lead is the best material for this purpose.

The cathodes are usually thin sheets of pure copper. In depositing copper from impure solutions derived from the leaching of ores it is found difficult to get a reguline deposit, unless considerable care is taken with purifying the electrolyte and the regulation of current density. Irregular deposition and sprouting may require the removal of the cathode before acquiring the desired thickness. With reasonably pure electrolyte and low current density, difficulty will not occur, especially if the electrolyte is agitated or the cathode removed. The current density and the nature of the electrolyte have much to do with the purity and the quality of the deposit.

Most electrolytic processes are based on the regeneration of the solvent during electrolysis. This requires that the anolyte and catholyte be kept separate. A diaphragm which will allow the current to pass, but prevent solutions from mixing, becomes necessary. Few materials for diaphragms fulfill the required conditions. They must be permeable to charge ions, prevent diffusion of electrolyte, and carry no current by metallic conduction. Asbestos is the best material, as it is not easily attacked by acid or alkaline solutions. It is used as cloth, paper or mill board.

The current density affects the efficiency of the operation and the nature of the copper deposited. It is not possible to use as high current density as in electrolytic refining, because of the impure and leaner solution. To get reguline deposit, operation at low current density is necessary. High current density causes impoverishment of ions at the electrodes, which may be prevented by stirring the electrolyte or by a movable electrode. Energy efficiency becomes less as the current density increases.

Wilde was one of the first to deposit copper on a revolving cathode. He secured an even distribution of

the copper. The current density was 20 amperes per sq. ft. (22 per sq. dm.). Elmore used horizontal mandrels. The current density was 30 amperes per sq. ft. (3.3 per sq. dm.). Cowper-Coles used a cylindrical cathode, revolving at a speed of 1,500 to 2,000 lin. ft. (450 to 600 m.) per minute, with a current density of 200 amperes per sq. ft. (22 per sq. dm.). (U. S. Patent 895,163, Aug. 4, 1908, Cowper-Coles; Greenawalt, p. 283 to 290).

Theoretical Data.—1 ampere-hour deposits from cupric solution, 1.1858 gr. copper.

1 ampere-hour deposits from cuprous solution, 2.3717 gr. copper.

12,000 ampere-hours deposits from cupric solution, approximately 32 lb. copper.

12,000 ampere-hours deposits from cuprous solution, approximately 64 lb. copper.

The theoretical voltage required for electrolyzing with insoluble anodes is: For cupric sulphate, 1.22 volts; cupric chloride, 1.35 volts; cuprous chloride, 1.53 volts.

The output in depositing copper from solutions with insoluble anodes is:

$$\text{Cupric sulphate, } \frac{32}{12 \times 1.22} = 2.1429 \text{ lb. per kw. hour}$$

$$\text{Cupric chloride, } \frac{32}{12 \times 1.35} = 1.9364 \text{ lb. per kw. hour}$$

$$\text{Cuprous chloride, } \frac{64}{12 \times 1.53} = 3.4174 \text{ lb. per kw. hour}$$

Illustration: There were used in precipitating copper from cuprous chloride solution 400 amperes per 12 hours (4,800 ampere-hours) at 1.8 volts. Copper deposited, 18.2 pounds. Theoretically there should be

$$\frac{4,800}{12,000} \times 64 = 25.6 \text{ lb.}$$

$$\text{Current efficiency, } \frac{18.2}{25.6} = 71.2 \text{ per cent (practice about 90 per cent).}$$

$$\text{There was deposited, } \frac{18.2}{4.8 \times 1.8} = 2.11 \text{ lb. of copper per kw. hour.}$$

$$\text{Energy efficiency, } \frac{2.11}{3.417} = 61.8 \text{ per cent (practice, about 50 per cent).}$$

For electrolytic refineries, Addicks gives a rough summary of the relative value of the resistances in practice: Metallic resistance 15 per cent, electrolytic resistance 60 per cent, contacts 20 per cent, counter E. M. F. 5 per cent. The counter E. M. F. in copper refining, due to greater concentration at the anode than at the cathode, is 0.02 volt. Copper refining employs 0.2 to 0.4 volt between the electrodes. Copper

depositing with insoluble anodes employs 1.5 to 3.0 volts, depending on the current density and concentration of the electrolyte. (Greenawalt, p. 295; The Journal of the Franklyn Institute, Dec. 1905, Addicks).

The solvents usually employed have sulphuric or hydrochloric acid as the basis. The cycle consists of: Solution, precipitation, regeneration. In a cyclic process the solution is likely to become charged with impurities and reduce the efficiency of the deposition.

The injurious effects of impure electrolyte are:

1. Undesirable metals may be deposited with copper, when the solution becomes impoverished.
2. Useless energy is expended in reduction and oxidation, deposition and immediate dissolving.

The metals whose compounds have the lowest heats of formation are first deposited. Gold, silver and copper come first, and are deposited in the order given. If the current density and, consequently, voltage exceed a certain amount, several metals may be deposited together. The more neutral the electrolyte, the more likely the more electro-positive metals (such as iron, nickel and zinc) are to be deposited. High current density may deposit copper and zinc together from slightly acid electrolytes. If much acid is present, hydrogen will be liberated, causing low efficiency. High current density may deposit copper and a more electro-positive metal not readily redissolved, producing impure copper. The practical factors which determine the kinds of ions deposited at the cathode are: Heats of formation of the constituents of the electrolyte, concentration of anolyte and catholyte, current density at cathode, temperature of electrolyte.

If arsenic and antimony were originally in the ore, they should have been largely eliminated by roasting. If they should accumulate in the solution, they may be precipitated by hydrogen sulphide, which, however, is expensive. Iron is most likely to be in the lixivium. In sulphate solutions the iron may accumulate by saturation, unless the solution is purified at intervals. With chloride solutions, more or less ferric oxide is precipitated by reaction with the ore. The influence of iron in the electrolyte may be summed up as follows:

1. Becomes oxidized to ferric salt at the anode.
2. Is carried to cathode by diffusion and circulation.
3. Dissolves precipitated copper, becoming reduced to the ferrous conditions.
4. Is carried again to the anode by diffusion and circulation, again becoming ferric iron.

This cycle continues indefinitely, greatly reducing the efficiency of the electric current. To economically precipitate copper from an electrolyte containing much iron, either a diaphragm must be used to prevent diffusion, or a reducing agent (acting as a depolarizer) must be introduced.

There are two alternatives relative to impure electrolyte:

1. Purification of electrolyte.

2. Wasting a portion of the solvent, and replacing with fresh solution.

Ulke states that the best method is to electrolyze in special vats with lead anodes and to use a current density sufficiently strong to deposit arsenic and antimony, but not strong enough to deposit iron. This is repeated till the bath contains so much iron that it is necessary to remove it by crystallizing out the ferrous sulphate. (Greenawalt, p. 300; "Modern Electrolytic Copper Refining," Titus Ulke).

Ottaker Hofmann gives the following method for purifying copper sulphate solutions containing as impurities salts of iron, arsenic, antimony, bismuth, etc.: The crude copper sulphate solution is forced into towers lined with lead and provided with a lead steam coil for heating. A lead pipe connected with an air compressor enters through the funnel-shaped bottom. When the solution is hot, roasted matte is added and air forced in, causing precipitation of the iron according to: $2\text{FeSO}_4 + \text{O} + 2\text{CuO} = \text{Fe}_2\text{O}_3 + 2\text{CuSO}_4$. To observe and regulate the progress of the operation the solution is tested for iron from time to time. When the solution is free from iron it will contain no trace of other impurities. (Mineral Industry, Vol. VIII, p. 192, Ottaker Hofmann).

At the Kalakent Copper Works, Russia, impure electrolyte was run over dead roasted matte, then over a heap of low-grade copper ore. The neutral solution was run into a lead-lined vat, where it was diluted to 12°B. and heated to 50°C. Scrap anode copper was hung in the vat to neutralize any acid found in the operation. Compressed air was forced in till the concentration was 15°Bé. , the scrap copper being quickly dissolved. The liquid was drawn off and clarified. The excess of purified electrolyte which gradually accumulated was withdrawn from the system and worked up into bluestone ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$). The copper produced was 99.9 per cent pure. ("Modern Electrolytic Refining," p. 145, Titus Ulke).

Copper sulphate may be crystallized out of impure solutions, redissolved in water and electrolyzed to deposit the copper, thereby regenerating acid which is applied to leaching the ore. The impurities are thus eliminated.

Greenawalt proposes purifying chloride solutions by electrolyzing sodium chloride, producing free chlorine and caustic soda: $\text{NaCl} + \text{H}_2\text{O} + \text{electric current} = \text{NaOH} + \text{Cl} + \text{H}$. Caustic soda is applied to a portion of the withdrawn electrolyte, causing precipitation of the bases according to: $\text{RCl}_2 + 2\text{NaOH} = 2\text{NaCl} + \text{R(OH)}_2$. (R represents the base metals). The chlorine is converted into hydrochloric acid: $2\text{Cl} + \text{SO}_2 + 2\text{H}_2\text{O} = 2\text{HCl} + \text{H}_2\text{SO}_4$. Thus the impurities are eliminated and the hydrochloric and sulphuric acid solvents are regenerated. (Greenawalt, p. 303, p. 352).

If impurities in the electrolyte do not materially interfere with the efficiency of the process, it is better to work with impure solution even though impure copper be deposited. The efficiency of the process is more important than the relative purity of the copper.

Cobly, in 1878, described the use of sulphur dioxide for the depolarization of insoluble anodes in the deposition of copper. Its operation in recent years is common and well understood. Other depolarizers have been suggested. (Greenawalt, pp. 283 to 309).

The following theoretical voltages were calculated by introducing Richards' thermochemical data in reactions, which we believe represent the operation of the electrolytic cells:

I. Deposition of copper from sulphate solution:

(a) Without using a depolarizer, $\text{CuSO}_4 + \text{H}_2\text{O} + \text{electric current} = \text{Cu} + \text{H}_2\text{SO}_4 + \text{O} - 56,300$ calories.

$$\text{Theoretical voltage, } \frac{56,300}{(96,540 \times 0.24 \times 2)} = 1.22 \text{ volts.}$$

(b) Using SO_2 gas as a depolarizer, $\text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O} = \text{Cu} + 2\text{H}_2\text{SO}_4 + 7,300$ calories.

$$\text{Theoretical voltage, } \frac{7,300}{(96,540 \times 0.24 \times 2)} = -0.15 \text{ volt.}$$

(c) Siemens and Halske process, using FeSO_4 as depolarizer, $\text{CuSO}_4 + 2\text{FeSO}_4 + \text{electric current} = \text{Cu} + \text{Fe}_2(\text{SO}_4)_3 - 16,800$ calories.

$$\text{Theoretical voltage, } \frac{16,800}{(96,540 \times 0.24 \times 2)} = 0.36 \text{ volt.}$$

II. Deposition of copper from cupric chloride solution:

(a) Without using a depolarizer, $\text{CuCl}_2 + \text{electric current} = \text{Cu} + 2\text{Cl} - 62,500$ calories.

$$\text{Theoretical voltage, } \frac{62,500}{(96,540 \times 0.24 \times 2)} = 1.35 \text{ volts.}$$

(b) Body's process, using FeCl_2 as a depolarizer: $2\text{FeCl}_2 + \text{CuCl}_2 + \text{electric current} = \text{Cu} + 2\text{FeCl}_3 - 7,000$ calories.

$$\text{Theoretical voltage, } \frac{7,000}{(96,540 \times 0.24 \times 2)} = 0.15 \text{ volt.}$$

III. Deposition of copper from cuprous chloride solution:

(a) Without using a depolarizer, $\text{CuCl} + \text{electric current} = \text{Cu} + \text{Cl} - 35,400$ calories.

$$\text{Theoretical voltage, } \frac{35,400}{(96,540 \times 0.24)} = 1.53 \text{ volts.}$$

(b) Hoepfner's process, using CuCl as a depolarizer, $2\text{CuCl} + \text{electric current} = \text{Cu} + \text{CuCl}_2 - 19,400$ calories.

$$\text{Theoretical voltage, } \frac{19,400}{(96,540 \times 0.24)} = 0.84 \text{ volt.}$$

In the above equations, where the minus sign (—)

precedes the numerical value of the calories, this sign means that the given number of calories is absorbed in the reaction and that their equivalent in electrical energy must be supplied from an external source, viz., the dynamo. Thus the calculated voltage is the necessary theoretical impressed electromotive force that must be supplied in order that the reaction may take place. When a depolarizer is used the required impressed volts are lower than when a depolarizer is not used. Compare equation I (c), 0.36 volt, with equation I (a), 1.22 volts. There is thus a saving of energy and also of expense in precipitating copper when using a depolarizer. This reducing of voltage due to using a depolarizer is realized more efficiently with low current density. The gas is then liberated at the anode at such a moderate rate that it will have a chance to react with the depolarizer, and not escape as such without reacting. In proportion as this reaction is more complete, so will the theoretical voltage be more nearly attained.

Referring to an experiment of K. Reinartz, recorded by Austin, Reinartz secured an anode efficiency of 65 per cent when using sulphur dioxide as a depolarizer. Thus 65 per cent of the oxygen liberated at the anode did react with the sulphur dioxide depolarizer. ("Metallurgie," 1908, pp. 202 to 205).

Equation I (b) works out with a (+) sign for the calories and gives (-0.15) volt. This would indicate that with such a current density as to secure anode efficiency of 100 per cent, if this could be realized, the electrolytic cell would no longer require an impressed voltage, but would become a primary cell. Of course, a dynamo would have to supply voltage to realize a current of any magnitude, but the cost of operating, were this high anode efficiency secured, would be as low as that of electrolytic refining. (Mines and Methods, Aug., 1911, p. 282, W. L. Austin, Reinartz Experiment).

I. ELECTROLYTIC SULPHATE PROCESSES.

There are two general classes of processes based on the solvents sulphuric acid and ferric sulphate. Neither of these solvents can be employed to the exclusion of the other. On certain copper sulphide ores, ferric sulphate solution has given good results without roasting. The necessity of using a diaphragm, or the introducing of a reducing gas such as sulphur dioxide when iron salts are present, has been mentioned.

Sulphuric Acid Process.—Only oxidized or roasted ores are effectively treated by dilute sulphuric acid. See equation I (a), where the theoretical voltage = 1.22 volts. The minimum voltage required is 1.22 volts. In practice 1.5 to 3 volts are employed.

Plant of Intercolonial Copper Co., N. S., Canada.—The process is: Roast ore to sulphatize the lime and oxidize iron sulphide to ferric oxide. Drop hot ore into 5 per cent sulphuric acid. Send the copper sulphate solution to storage tank. Blow in sulphur dioxide. Send reduced solution to electrolyzing tanks,

which are arranged in cascade. Force sulphur dioxide into electrolyte through hard rubber tubes; the gas acts as agitator. The anodes were slowly sulphatized, much less rapidly than they would have been peroxidized were SO_2 absent. Current density 6 amperes per sq. ft. Voltage, 1.5 volts. Electrodes spaced $1\frac{1}{2}$ in. apart. Current efficiency 90 per cent. The solution enters the electrolyzer with 2.5 per cent copper and leaves with 1 per cent copper. The process is cyclic, continuing indefinitely. Ore contains 2.5 per cent of copper, and tailings 0.1 per cent. (Greenawalt, p. 316; Electrochemical Industry, April, 1903).

Tossizza Process.—Ferruginous copper sulphate solutions are electrolyzed while introducing sulphur dioxide into the electrolyte. The voltage is so adjusted that copper is deposited without affecting the iron. Voltage 0.2 to 0.6 volt. (Greenawalt, p. 330; U. S. Patent No. 710,346, Sept., 30, 1902.)

Siemens-Halske Process.—The ore is ground fine and roasted at moderate temperature. It was the intention of the inventor to so roast that most of the iron would be converted to ferric oxide, while most of the copper would remain as cuprous sulphide. This operation could not be performed. An equally satisfactory roast can be obtained when conducted at a moderate temperature (450°C. to 480°C.), most of the copper being converted into soluble sulphate. Do not roast at a high temperature (dead roast), because much cupric oxide would combine with silica to form silicate, and with ferric oxide to form ferrite, which are difficultly soluble compounds. The active solvent of the process is ferric sulphate, which should dissolve all the cuprous sulphide left undecomposed during the roasting. In the operation of this process, ferric sulphate becomes reduced to ferrous sulphate. In the electrolytic cell the ferrous sulphate acts as a depolarizer with regeneration of ferric sulphate. A diaphragm is used between anodes and cathodes. See equation I (c); theoretical voltage = 0.36 volt. In experimental tests, impressed voltage used varied from 0.75 to 1.8 volts. This process is not in practical use. (Greenawalt, p. 319).

Experiments at the Ray Mines, Arizona, by W. Y. Westervelt.—The ore at Ray mines is a great body of disseminated sulphides. The process decided upon for the experiment was along the lines of the Siemens-Halske process. One ton of 2.5 per cent copper ore was treated. Extraction, 80 per cent; 1.06 lb. Cu was produced per kw. hour. Cost of copper per pound, 4.5 cents, which included only the operating expense. When charged with mining, transportation, etc., the cost would be 14.5 cents per pound of copper. (Greenawalt, p. 327; Mines and Methods, Oct., 1910, W. L. Austin).

2. ELECTROLYTIC CHLORIDE PROCESSES.

There are three general classes of processes based on the solution hydrochloric acid, ferric chloride cupric chloride.

The Body Process for the Extraction of Gold, Silver and Copper from Ores.—This process, patented in Belgium in 1883, is of interest historically. The ore is ground fine and roasted. It is subjected to the action of ferric chloride solution while an electric current is simultaneously passing through. The metal becomes dissolved, and is precipitated at the cathode. Chlorine liberated at the anode reconverts ferrous to ferric salt. Note that, theoretically, the effect of the ferrous chloride depolarizer is to reduce the required impressed voltage from 1.35 [called for by equation II (a)] to 0.15 volt [that called for by equation II (b)]. (Greenawalt, p. 340; U. S. Patent 333,815, Jan., 1886).

The Hoepfner Process.—Cupric chloride, together with sodium or calcium chloride, is used as the solvent. The ore is ground fine and treated with the cupric chloride solution, which becomes reduced to cuprous chloride. The solution is then split in two streams, one passing through the anode compartment and the other through the cathode compartment. The anode stream acts as a depolarizer and becomes regenerated to cupric chloride, while the copper is precipitated from the cathode stream. On issuing from the electrolyzer the two streams are reunited and constitute the regenerated solvent, containing, one-half the copper contents of the original stream. A diaphragm separates the anode and cathode compartments. Note that, theoretically, the effect of the cuprous chloride depolarizer is to reduce the required impressed voltage from 1.53 [called for by equation III (a)] to 0.84 volt [that called for by equation III (b)]. It is claimed for this process that practically 0.6 to 0.8 volt is required. This process was used at Schwartzenberger Hütte, in Saxony, from August, 1891, to March, 1892. The results were unsatisfactory. The main difficulty appears to be metallurgical, the cupric chloride being a somewhat indifferent solvent. The question arises, "Would this process not work better on roasted ore?" (Greenawalt, p. 342).

Leaching Experiment on Keystone Ore at Miami, Arizona.—The ore contains 3 to 5 per cent of copper, occurring on the surface in veinlets of chrysocolla ($\text{CuSiO}_3 + 2\text{H}_2\text{O}$) in white porphyry. It was desired to employ a process in which the solvent was regenerated and which produced marketable copper. The process used for experiment was a modification of the Hoepfner process. The ore crushed to $\frac{3}{4}$ in. (2 cm.) was first treated in a kiln, wherein it was subjected to the action of reducing gases from a small gas producer. The reduction was fairly complete, almost all the copper appearing in a metallic state in the calcined product. The lixiviant contained 5 per cent of copper as cupric chloride, and 20 per cent of sodium chloride. Calcined ore, 12 mesh, treated with hot leaching solution for 2 hours, gave 83 per cent extraction; 60 mesh, 99 per cent extraction. Electric light carbons were used for anodes. The potential employed per cell was 1 volt, with current density of 10 to 12 amperes per

sq. ft. (1.1 to 1.32 per sq. dm.). One ton of copper was produced. The final washings from the leaching barrels were run over scrap iron, and the cement copper was used to reduce the last of the cupric chloride to cuprous chloride in the lixivium before going to the electrolytic cell. (Mines and Methods, Nov., 1911, p. 355, Leaching Applied to Copper Ore, W. L. Austin).

The Greenawalt Process.—The copper in the ore is dissolved by dilute acid chloride solution and precipitated by electrolysis. The acid is regenerated and augmented at the expense of sulphur dioxide and water. In practice, there is required to be supplied 2 ounces (58 grams) of salt per pound of copper extracted. Since the copper in the electrolyzer is in the cuprous state, twice the amount is deposited for a given amperage. The process may be applied to the following ores: 1. Siliceous oxidized copper ores. 2. Siliceous sulphide copper ores. 3. Copper concentrates. 4. Siliceous gold and silver ores containing copper.

Greenawalt claims that for treatment of No. 4 ores there is no other satisfactory process. If there is much iron in the ore, it is desirable to roast. Sulphide ores necessitate roasting. In treating these various ores experimentally an extraction of 90 to 98 per cent of total copper, gold and silver contents has been obtained. Theoretical impressed voltage was 1.53 volts. (See equation III (a).) Copper is deposited 1 lb. per kw. hour. The estimated cost of producing copper is 2.7 cents per pound, administration expense not included. (Greenawalt, p. 349; E. and M. Journal, Nov. 26, 1910; U. S. Patent, 673,776, Oct. 25, 1910).

The Recovery of the Gold and Silver Contents of Copper Ores.—Most copper ores treated by wet methods contain valuable amounts of gold and silver, the recovery of which is important in many cases. While the assay returns may be practically *nil*, the aggregate recovery in a year may be considerable. Utah Copper Company during the year 1910 recovered on an average 23 cents value in gold and silver per ton of ore treated.

The gold and silver may be recovered: (a) Before the copper is precipitated; (b) simultaneously with the copper; (c) by a subsequent operation.

(a) With the Hunt and Douglas process, when the leaching is done with ferrous chloride and salt solution, silver is converted into AgCl by CuCl_2 . After reducing all copper to the cuprous condition the silver may be precipitated on copper.

(a) and (b) In Greenawalt's U. S. Patent 973,776, when there is gold in the ore he increases the free chlorine in the lixiviant, and thus both gold and silver are dissolved. Then leaching with fairly concentrated solution of base metal chlorides, dissolving both the gold and silver with the copper, the gold and silver may be precipitated prior to, or with the copper, by varying the current density.

(a) and (b) In the Bradley process the gold and silver are brought into solution, and may be precipitated with the copper, or separately.

(b) The Longmaid-Henderson process, while formerly precipitating the silver prior to copper, now precipitates them jointly, since the electrolytic refineries pay for 95 per cent of silver and all of the gold and copper.

(c) In the Hunt and Douglas process, when leaching roasted ore with dilute sulphuric acid, the gold and silver are left in the residue. Silver is extracted by brine, and gold by chlorination, amalgamation or cyanidation. (Mines and Methods, March, 1912, p. 433, Leaching Applied to Copper Ore, W. L. Austin).

SUMMARIZING AND LOOKING TOWARD THE FUTURE.

A number of important copper mining companies are experimenting with the development of hydrometallurgical methods. Mr. Laist, at Anaconda, expects to produce copper for 6.5 cents per pound from concentrator tailings. There are two concerns in Butte, Montana. The Butte-Duluth Company and The Bullwhacker Company, which are producing finished copper on a commercial basis. Throughout the Southwest experimenting is being conducted. The Arizona Copper Company, at Clifton, Arizona, has been using leaching methods for treating concentrator tailings of their oxide mill for many years. The recent experiments of the Shannon Copper Company, at Clifton, Arizona, with a view to reducing acid consumption on an ore with a basic gangue, are very encouraging. The Braden Copper Company, Chile, is experimenting, leaching one-fifth of their output of concentrates. The Chile Exploration Company is extracting copper from an ore which is very amenable to leaching. Spain, Germany, England and Russia have commercial plants or are experimenting in this field.

It is said there is hardly a known chemical reaction which has not been applied. It would appear that no method of universal application is likely to be developed, that present methods will be perfected, and that the one most suitable will be selected for the particular case.

Passing the different methods of extraction in review, we may generalize:

I. Dissolving the copper.

II. Precipitating the copper.

I. (a) In completely oxidized ores, by crushing and leaching with dilute acid direct.

(b) In a mixture of oxidized and sulphide ores, by sulphatizing or chloridizing, roasting, and leaching with dilute acid.

(c) In straight sulphide ores, by sulphatizing or chloridizing, roasting, and leaching with acid.

(d) In ores, by a modification of (a), (b) and (c), taking advantage of the solvent action of solutions containing ferric salts.

II. (a) Precipitating by chemical reagents.

1. Iron—cast iron, sponge iron, scrap iron.

2. Lime.

(b) By electrolytic deposition, with insoluble anodes of graphitized carbon for chloride solutions; and peroxidized lead anodes, or magnetic oxide anodes

for sulphate solutions. (Fe_3O_4 anode, made by fusing magnetite, and casting).

The precipitation of the copper will be:

1. From pure or purified electrolyte (one free from iron salts).

2. From ordinary impure electrolyte, using sulphur dioxide as depolarizer without a diaphragm, and securing (a) regeneration of acid solvent and (b) high current efficiency and high energy efficiency.

3. From ordinary impure electrolyte using ferrous salt with a diaphragm as depolarizer, regenerating the ferric salt as a solvent and securing high current efficiency and high energy efficiency.

There are two important economic considerations which alone should goad the metallurgist to future discoveries in hydrometallurgical methods:

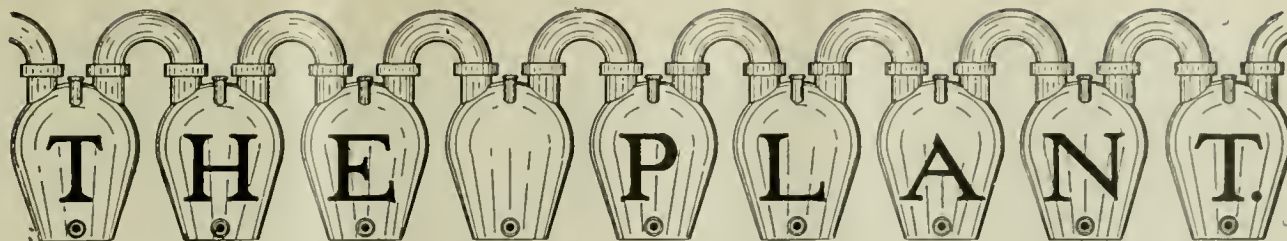
1. Enhancement of the life and value of a property 50 per cent when the hydro-metallurgical process extracts 90 per cent, as against 60 per cent by the combined concentrating-smelting process, assuming equal cost per pound of metal produced in the two cases.

2. Possible treatment at a profit of certain complex mineral-aggregates not otherwise amenable to extraction, recovering the several metals.

Articles not previously accredited: W. L. Austin's numerous consecutive articles in Mines and Methods, Sept., 1910, to Oct., 1912; E. and M. Journal, Oct. 4, 1913, Vol. 96, No. 14, p. 651, Leaching of Copper Ores; E. and M. Journal, Nov. 22, 1913, Vol. 96, No. 21, p. 962, Copper Leaching; Mining World, May 17, 1913, Vol. 38, No. 21, p. 947, Baxeres de Alzugaray, Extension of Hydro-metallurgical Industries; Mining and Scientific Press, July 19, 1913, Vol. 107, No. 3, p. 127; Mining and Scientific Press, Aug. 16, 1913, Vol. 107, No. 7, p. 252, Sulphuric Acid Leaching; Metallurgical and Chemical Engineering, 1913, p. 600, Leaching Copper Ores and Tailings.

Credit is also due to Dr. Edward F. Kern, of the Metallurgical Department of Columbia University, for kindly looking over the manuscript and offering suggestions.

The excessive shrinkage of brass or bronze alloys necessitates a core which will be crushed readily by the molten metal, according to the *American Machinist*. Large cores should be made with a soft interior, and this is generally accomplished by filling the interior of the core with cinders, powdered coke, or similar material. The core material must be fine, and this requires the use of finer sands for brass-foundry cores than those usually used in iron foundry work. When a brass casting has been poured and is shaken from the mould, care should be taken to keep the core sand from mixing with the molding sand. The cores for brass and bronze castings are sometimes blown out by shaking out the molds while the castings are still fairly hot, and then dipping the castings in water.



HYGIENE IN LEAD SMELTING.

By H. B. PULSIFER.

The recently issued Bulletin 141 of the United States Bureau of Labor Statistics entitled, "Lead Poisoning in the Smelting and Refining of Lead," brings to the front a phase of the metallurgy of lead never before seriously considered in this country.

The bulletin discusses the methods and equipment in the smelting and refining of lead; it shows that dust and fume are largely uncontrolled and free to afflict the workmen; the bulletin indicates the poisonous nature of the lead and arsenic compounds with a new investigation which establishes the solubility of galena in gastric juice and puts it in the list of poisonous compounds; the bulletin hints at the inability of the laborers to improve their circumstances and discloses the habitual tendency of plant managers to neglect and conceal the condition of their workmen; finally, the bulletin publishes the number of cases of poisoning found and shows that the percentage of men afflicted is beyond reason, larger here than in other countries, a total of 1,769 cases out of an average payroll of 7,400 men during 1912; finally, the bulletin indicates the simple and necessary conditions required to prevent most of the entire trouble.

Too much credit cannot be given Dr. Alice Hamilton, of Hull House, Chicago, for the successful issue of such an investigation. Without technical training, and exposed to all the obstacles which managers and superintendents intended should block the work, she persevered until two-thirds of all the plants in the country had been visited and the startling facts, one piling on another, accumulated to witness the great and unnecessary evil. What the plant owners would not attend to, a matter which the engineers have passed over lightly, a topic which employes were in no position to champion, this outsider has dug into and proven to be of the most serious import. She has not only procured the facts and marshaled them in convincing array, but, issued as a government bulletin, they are coming to the attention of a great many people. S. J. Gompers, chief of the Division of Publications and Supplies of the Department of Labor, says there is "an immense demand for this bulletin."

In an industry which has 22 out of every 100 men suffering from lead poisoning and which is supposedly under chemical control, one might be led to think that this great affliction were something too subtle for mod-

ern science or too baffling for our chemical engineers. The consensus of study, both in Europe and here, is that only the over-susceptible are liable to poisoning *if cleanliness is enforced and dust and fume are suppressed.* With only this simple expedient necessary, it is our inevitable conclusion that the chemist and the chemical engineer have a limited scope in the lead plants.

THE SUBMERGED CHEMIST.

Our observation is that the chemist employed in such industrial work is more properly called an analyst and the place he labors in more properly designated by a term of his own coining rather than the word laboratory. Such terms actually used are "sweat shop," "pen," "cage," "jail," "prison." The author quite unexpectedly was once remanded to one of these places for a limited period; his accuracy was likely passable, as good as the rest or as good as required, and for speed he was complimented. One particular day's run was jotted down in the notebook for later reference; it is thus summarized for the two men at work that day:

Leads on regular ores.....	31
Leads on slags.....	12
Leads on fire assays.....	7
Coppers	18
Insolubles	28
Irons	20
Limes	6
Manganeses	3
Zincs on regular ores.....	18
Zincs, special	8
Silicas, fusion	2
Silicas, Als, Fes, Cas, etc., on slags.....	18

171

These 171 determinations cost the company \$0.0415 apiece for the labor alone, possibly 6 or 7 cts. apiece, everything included. We had the usual busy 10-hour day; the author's pay was \$3.00; the head chemist got \$4.10. Less skillful bricklayers in the same plant at the same time made \$5.00 during less hours. The plant was a large western lead smeltery under good sampling and chemical control for *operating purposes only*; the author was at various times admonished that the crew was there to *operate*, that suggestions or improvements were decidedly out of order.

When a graduate chemist goes into such a plant to stay, he debases his vocation while, at the same time, his employer spurns one he will eventually need most sadly.

HYGIENE A NEGLECTED FACTOR.

A closer study of this vicious condition which neither employer, operator, chemist nor laborer has cared or been able to better resolves itself into a matter of the various equipment units which are found in the plants in question. We shall find that the furnaces and machines of the lead plants have been evolved without any particular reference to the dangerous properties of the material to be handled; even more than this, the diverse units have been and are operated without any adequate accessory provisions for removing or suppressing the noxious fume and dust incidentally dispersed during the active processes.

The great bulk of the iniquity arises from letting dust and fume escape from machine and furnace to pollute the air the men breathe, to soil garments and exposed skin of the men, to accumulate on walls and floors and every material object ready to again dislodge for the discomfort of the men. The matter is then, to keep dust out of the working spaces, to keep the dust within a system which men do not have to enter; it is the same for the fume. In a large measure the lead industry has accomplished this very condition for the purpose of saving values and preventing wholesale pollution of the surrounding country in the case of the bag house; it now remains to carry this principle a step farther, to make it cover every detail and completely, in particular to make the dust and fume disposal system sufficient for the *extraordinary* occasions which inevitably arise.

The matter of cleanliness in lead plants is not satisfied by providing an elaborate wash room alone; it is true that the facility must first exist but to effect observance is a matter of education and lasting insistence. The entire supervising staff in any lead plant should be held responsible for this detail of safety. We believe that the simple washing of hands and face before eating will be one of the easiest reforms to bring about; whenever the management of a plant makes it a point to have the order passed along and insisted upon. The fact is that up to the present the supervising force in most plants has troubled little about keeping the workmen safe from this danger. No boss or foreman will lay himself open to criticism from his superiors by insisting on cleanliness even if he personally recognizes the danger to his men. On the other hand, when the order comes down from above as a clean cut matter of safety to be instilled into the workmen and everlastingly persisted in, progress will be accomplished. In view of the regulations in certain states on this matter of wash rooms some plants are already splendidly equipped with elaborate buildings for the purpose. The staff at such plants might make one think that altruism was their great virtue, that they spent a few thousands on their own initiative to conserve their men; we might whisper that they are trying to steal the thunder of the reformers, that before Dr. Hamilton came at them through state regulations they were innocent of any such ideas.

The general course of ore entering a lead plant is outlined in the following main operations: sampling, bedding or storage, ore hearths or blast furnaces or roast-sintering machines, from which singly or in combination issue metallic lead and slag as the two great end products with matte and flue dust and fume as the by-products which return to the system.

SAMPLING LEAD MATERIALS.

The process of sampling is quite a complicated subject; we will not attempt to mention more than a few details. Fig. 1 shows the feed spout from main hopper to crusher; down one or the other of these chutes the stream of ore tumbles as the gate is cautiously raised by the crusher feeder. The author has stood at this spout to regulate the feed when the ore was frozen and encased in ice, under such conditions a continual fight to get the slippery boulders to grip and crush between the jaws of the crusher; at one time cars of perfectly dry ore came to go through, then the whole room would be filled with the heavy dust but one dare not leave the treacherous stream lest it come too strong and choke the crusher.

The engineers of today are mastering conditions a thousand times more difficult than to master the mechanical and dustless feeding at such a place. Mechanical feeders are everywhere coming into use and with proper inclosure and sufficient exhaust such a place need produce no nuisance in any room.

On one of the upper floors of the same sampling mill is a set of rolls as seen in Fig. 2. The spout from the sampling device above is partly inclosed—enough to keep the falling stream from spattering about too much. But the trough immediately feeding into the rolls is open and the machine, itself, is only partially inclosed. There is absolutely no idea of suppressing dust or of eliminating it from the working space.

In this same mill it is usually necessary to clean all the apparatus with compressed air between lots; again the dust is dislodged and relodged and how shall the cleaner get away from his own nuisance. They use "aspirators" to filter the air one breathes. Whoever has seen or used one knows that such an apology can never settle the issue.

There is not the slightest doubt but that sampling mills are this very moment in the heat of evolution; every year they are built better, more scientifically, more automatically, of greater tonnage and to operate at less cost per ton capacity. Sampling mills have been a feature of the western lead smelting industry and in studying many such structures one finds abundant room for improvement both as a milling, sampling, and sanitary arrangement. They can be made to operate cheaper and yet without dust. The clouds of dust which today are blown about or thrown into the discard may tomorrow be treasured and proportionally put into the final sample as representing an actual part of the material bought and sold. It is no idle dream to think of collecting every bit of this dust in an appropriate filter, thus insuring that the seller shall

not lose from the assay samples even the least fraction, due to escape of some of the richer stuff.

The same argument applies to all classes of sampling and the further working up of mill and floor samples to the final assayers' packets. The bucking rooms of today are all too dusty and unnecessarily so. Spraying with water palliates the evil but does not dispose of it. The handling of damp ores requires further precautions while muddy material is hardly to

it also is a natural sequence of the obvious impossibility of getting the layers uniform, or even the same layer of unvarying composition. The composition of the bed changes during the drawing of the bed while at the start and at the very end it is rank guesswork.

We hold that it will be for the real technical advance of not only the hygienic aspect and the handling cost, but far greater improvement in blast furnace metallurgy when the accurately sampled and analyzed



Fig. 1—Crusher Feed Spout in Sampling Mill, Entirely Open.

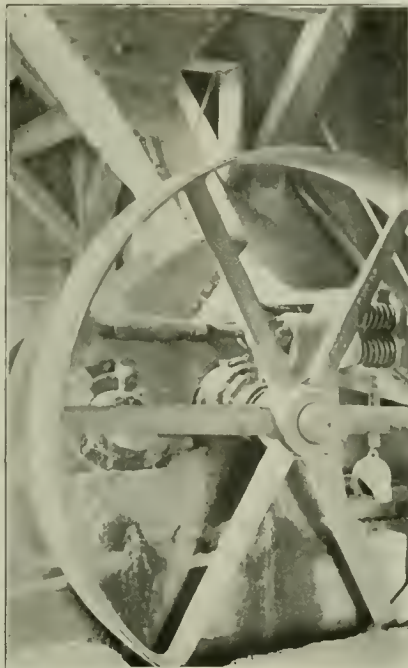


Fig. 2—Rolls in Sampling Mill (a Vicious Source of Dust).



Fig. 3—Ore Hearth With Flying Canopy.

be considered in this decade. Dry ores will absorb a great deal of water before really damp; it is certainly good practice to kill as much of the dust as practicable. Nevertheless, there is no total elimination of dust without making mud, and present or prospective plants are not designed for handling mud.

STORING AND BEDDING.

The operations involved in the bedding and storage of ores are essentially of a purely mechanical nature. In the coal industry, the iron and copper industries, and numerous other heavy tonnage propositions highly perfected mechanical arrangements and equipment cuts hand labor to the ultimate point of merely operating the machinery. If it is said that the lead smelteries require a finer adjusting of a small-lot and heterogeneous supply is it not simply a matter of intelligence and design to even improve on the finesse of hand labor. The actual spreading of lots of ore in thin layers over each other in the customary bin which may hold up to 3,000 tons is by no means an entirely satisfactory procedure metallurgically, whatever its shortcomings from the hygienic and operative sides. There is more than likely to be error in the sample of the completed bed; this follows from the impossibility of sampling properly such a mass *in situ*;

lots will each be deposited in its own bin or hopper by gravity and again drawn by gravity chutes or mechanical feeders to unite with the other similarly selected and gauged components on a trunk conveyor to go up to the furnaces. Several plants have just such an arrangement for assembling the charge for their roast-sintering machines; the same positively in practical use. Whenever this is done for the whole plant, including the blast furnace feed, there will be bettered, if not eliminated, one more condition dangerous to the health of the laborers.

SMELTING IN THE ORE HEARTH.

The author has been able to see all the ore hearths operating in this country and this, by the way, is no insignificant metallurgical treatment for nearly a third of the lead we make passes over such a furnace. This topic has been presented rather fully in a series of papers (Mining and Engineering World, March 7, 14, June 20, 1914) which emphasize the most important phases of this sort of ore treatment. The author firmly believes that the ore hearth is holding a false position in the industry today; that there is no reason why other and more mechanical means cannot be found to do the same work at a less cost and more humanely.

But if the ore hearth is to remain it is merely a matter of ordinary care to see to it that the workmen are not exposed to their own and the fume from all the rest of the hearths. Our Fig. 3 shows one out of a long line of hearths, there is a show at fume control in the outer and overhead canopy; this has by no means the real value of the hood seen in Fig. 4; the latter arrangement is in a hearth bay which has only five hearths, all told, and comes low enough to effectively control the air currents.

The great principle of fume control, patent to those who have seriously studied the subject, is that the air currents must be *controlled*. The providing of great open spaceways with huge volumes of passing breezes



Fig. 4—Snug Ore Hearth Boy.

is no control at all; it is an attempt to dilute and disperse, in which attempt everybody suffers from the dispersion. Long hearth bays should be divided up into short sections and then the ventilating currents must be held to definite and limited courses.

PREPARING LEAD ORES.

The introduction of roast-sintering in the metallurgy of lead was for some years represented wholly by up-draft or positive pressure apparatus. The inevitable result of blowing great quantities of air through the red hot and roasting leady material was to make greater volumes (due to increased temperature) of fume bearing gas. Engineers blew in air at out-of-door temperatures under about 12 ozs. pressure through a 6 in. pipe and expected the *heated* exit gas to escape through a 24 in. pipe under a fraction of an ounce suction. Whenever the charge choked the blast sufficiently the outlet would care for the gas, and whenever channels opened enough to let through much blast the exhaust would be flooded and fume and gas

might escape in great quantities to sweep the working space. Writers have commented on the hygienic deportment of such equipment; an experience of some years at daily observation convinces one that the system is inherently bad unless greater allowances are made for safety than are at present in use.



Fig. 5—Roast Sintering Machine in Operation.

The down-draft system, or roasting by suction, makes trouble of the sort just mentioned decidedly restricted. It is a great advance from the sanitary side. The moistened and dustless material comes in at the head of the machine, the roasting takes place with no appreciable escape of gas or fume while the



Fig. 6—Blast Furnace Front Without Hood.

roasted cake breaks off into the car without human assistance. Our Fig. 5 indicates exactly this condition. It shows the fumeless and dustless course of the material from the hopper at one end to the car at the other.

But even the best designed apparatus can be made to work viciously. In Bulletin 141 Dr. Hamilton complains that no installation of this sort is entirely faultless; her description of one plant indicates what a

mess can be made of an inherently excellent machine. Page 33:

This is much the worst Dwight-Lloyd building in the country. The lowest floor is covered with flue dust because the flues running through here are emptied from hoppers. Heaps of it lie about waiting to be mixed into charges for the machines. The second floor where the empty grates pass down is extremely dusty. The grate cleaner stands under the belt of grates, cleaning them with an air hammer. As there are many machines in a row, the air is full of dust from the cleaning. On the upper floor, where the roasting goes on, the dust is thick, but there is very little SO_2 . There is a hood over the flame, but it is only a fire box with no exhaust, and it is easy to see the fumes escaping under the edge. Out on a balcony near the discharge lie heaps of poorly sintered ore; two men stand on the balcony breaking apart cakes which

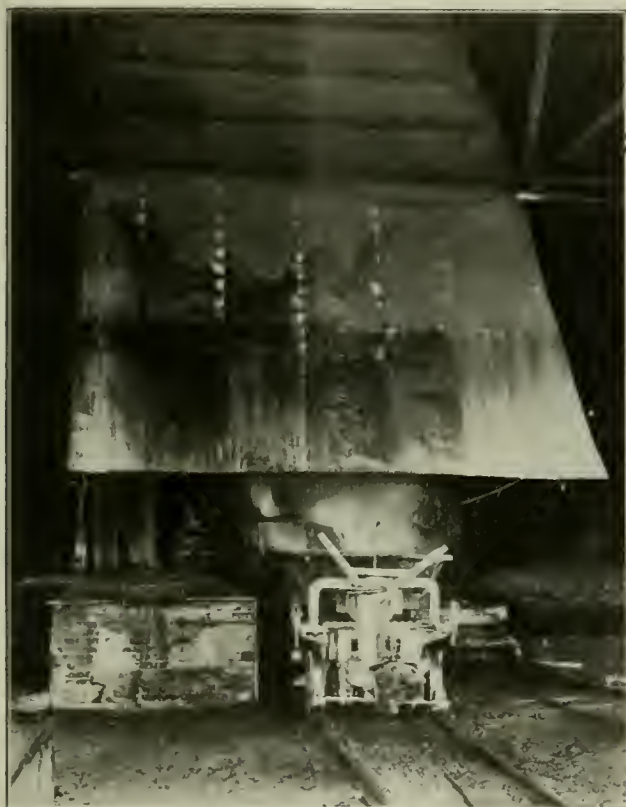


Fig. 7—Pretentious Blast Furnace Hood.

have stuck together, and on a platform below stand two more men to detach the cakes and make them drop into a car below. No water is used here, and there was so much dust in the air that after half a minute out on the balcony the paper of a notebook was covered with dust. On the top floor the conditions are rather better, for there is no dust where the charge comes down on the grates. The floor, however, was very dusty. A man was eating his lunch up there and the lunch pails of the other men were standing all about. There is no water for washing in this building.

BLAST FURNACES.

The feed floor of American blast furnaces is notoriously not only a terrible but a dangerous place. Some plants have reputations worse than others, we know of none where particular provision is made to meet the conditions that arise on occasion. After working for several months as foreman on one of these floors at one of the largest plants the author

planned construction which would meet the requirements at the worst of all times—when furnaces are blown out. Needless to say the company had not the slightest interest in such matters; the assistant superintendent had no authority, the superintendent had no interest other than routine operation, the manager being unapproachable on such subjects.



Fig. 8—A Fairly Good Blast Furnace Hood.

Pictures of blast furnaces in eruption would resemble volcanic outbursts. Billowy clouds of fume, sometimes white, sometimes black, surge from every opening of the floor and rise upward or are blown to one side in immense volumes. Men are compelled to quit the floor and seek air outside. Such matters are not of everyday happening, but may occur at all too frequent intervals in some plants; they preferably happen at night.



Fig. 9—Excellent Blast Furnace Hood.

But what is of routine nature in many plants is a floor continuously pervaded with fume dribbling from the mouths of one or more furnaces, or endlessly swept by the fume arising from operations on the tapping floor below. This whole matter we hold to be entirely removable by a very small amount of attention from the proper officials of the companies. A little interest, a small amount of construction and a mere suggestion

to the foremen involved will accomplish all that is required.

At the front of the furnaces is again a place where much unnecessary fume may originate. We present a series of four prints showing the present progress along this detail. Fig. 6 is of the front of a blast furnace which is quite unprovided with fume arresting hood; operators are seldom so brazen as not to make



Fig. 10—Reverberatory Furnace, No Hoods or Fume Control.

more pretense in these days. Fig. 7 is of a pretentious hood over the forehearth; it is to be noticed that the fume from spout, forehearth and pot is obligingly rising and disappearing up the proper flue. We will leave to the imagination what is the appearance when a strong breeze sweeps in or across the open front of the building. Fig. 8 is better than the last, for, although the hood is not as low it comes entirely down



Fig. 11—Hood Above Working Doors of Lead Reverberatory.

on one side. Fig. 9 shows a hood of the most recent construction. In the latter case the sides (at least one) come to the ground and the front is so low as to barely pass the pot and forehearth. It is noticeable what a small amount of the right construction protects the entire front and the feed floor as well.

REVERBERATORY FURNACES.

Reverberatory furnaces treating lead ores, metallic lead or leady by-products are even today generally

built without the slightest hint of any provision for fume elimination. Fig. 10 shows just such a condition; similar scenes are to be found in every plant having lead reverberatories. The dust made during charging, the fume during skimming and the gas escaping during heats can poison the tenders or float about the building to harm the others. Fig. 11 is a very recent hood construction over a softening furnace; Fig. 12 is a similar hood over a refining furnace. Both views indicate the simplicity of making nominal provision for the workmen; quite likely real efficiency would require larger section for the uptake pipe.

HANDLING MATERIALS.

Besides the specific operations involved in the receiving, sampling, bedding, roasting, smelting and refining of lead, such as already spoken of, every plant finds times and places where dangerous material must be moved. Furnace barrings, flue dust, bag house dust, arsenious oxide and grate cleanings are such

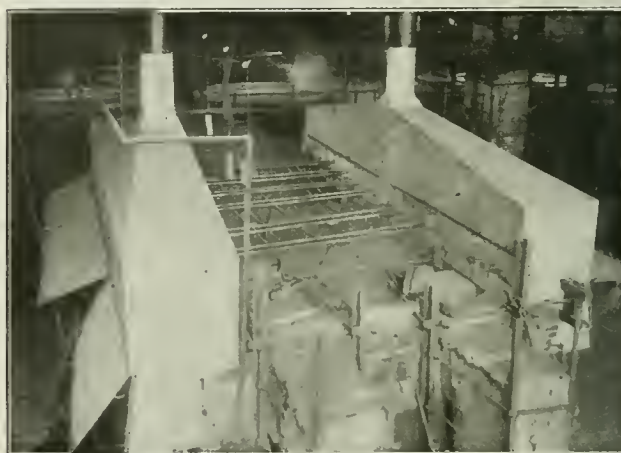


Fig. 12—Heads Over Lead Reverberatory (Refiner) Seen from Above.

materials. In 1911, at Midvale, Utah, the first rational method of removing bag house dust was initiated; this ought to be but the beginning of a long series of improvements, at once cost-reducing and hygienic, which are badly needed in the industry.

In bag house practice the Midvale plant has been an ornament to the industry; it originated and still uses the method of filtering roaster gases, it introduced pneumatic shaking of the bags, it started the screw conveyor system of removing the dust from below the bags.

In the furthering of the metallurgical and sanitary development there is probably no field so visibly accessible as this to the chemical engineer. Efficiency of operation, decreased cost, improved hygiene go hand in hand. Every betterment of working condition reacts quickly on stability of labor, the good will of the men, improved service. If the managements of the lead smelting companies are closing their eyes to the situation it is but evidence of their lack of acumen. The smelting companies can afford to keep ahead of

critical legislation. If they do not keep ahead of legislation they will be burdened with false smiles when the change is made and its value demonstrated. Within recent months several superintendents have with pride shown their new wash buildings and utterly ignored the work of Dr. Hamilton and recent state laws.

At this very moment we have in the milling, smelting and refining of lead a whole industry spread out like a new, rich, and untilled field, ready for the young man of chemical and engineering training to first master, then improve. There is not a plant in the country where his services are not needed; some plants can well support a dozen such apprentices. The proprietors of the plants have no reason to be prejudiced against the would-be chemical engineers; if they cannot prove their worth let fresh ones have the chance; of the many who try a few will succeed and by building change on change the whole industry transforms.

The ideas of personal cleanliness, eating with clean hands in a clean place, changing clothes and bathing the whole body is a matter between manager and worker which demands the manager's leadership and tact to enforce; the problems of suppression and elimination of dust and fume are up to the manager and engineer; the whole spirit of engineering and hygiene is a particular and unique opportunity for the chemical engineer.

According to a recent Government report the total quantity of Portland, natural, and puzzolan cement produced in the United States last year was the greatest in the history of the cement industry. The total amount was 92,949,102 bbls. valued at \$93,001,169, compared with 83,351,191 bbls. valued at \$67,461,513 in 1912. The total production of Portland cement in 1913, as reported to the Geological Survey, was 92,097,131 bbls., valued at \$92,557,617; the production for 1912 was 82,438,096 bbls., valued at \$67,016,928. Of the 113 producing plants in the United States in 1913, 23 were in the State of Pennsylvania, whose output was 28,701,845 bbls. of Portland cement, the largest quantity produced by any one state. The second greatest production came from Indiana, with 10,872,574 bbls., and California was third, with 6,159,182 bbls. The natural cement produced in the United States in 1913 amounted to 744,658 bbls. of 265 lbs. each, valued at \$345,889, compared with an output of 821,231 bbls., valued at \$367,222, in 1912. Puzzolan cement was manufactured in 1913 at three plants in the United States, in Alabama, Ohio, and Pennsylvania. The output of puzzolan and Collos cements in 1913 was 107,313 bbls. valued at \$97,663, compared with 91,864 bbls., valued at \$77,363 in 1912. The United States has a comparatively small export trade in cement. In 1913 the total quantity exported was only 2,964,358 bbls., most of which was Portland cement, valued at \$4,270,666, compared with 4,215,232 bbls., valued at \$6,160,341, in 1912.

CHEMICAL METHODS FOR UTILIZING WOOD WASTES.*

By W. B. CAMPBELL.

The fact that tremendous quantities of wood are wasted in Canada is well known to everyone. The waste begins in the forest and continues all through the various operations which the wood must undergo before it reaches the consumer in its finished form. Every time the wood is handled a greater or lesser amount of it is lost in some form of waste. Much of this waste is necessary at the present time, but on the other hand a great deal of the waste material can be put to use even now. Moreover, as the timber supply becomes depleted and the incentive to save becomes proportionally greater, a great deal more of this waste will be utilized and will become an economic asset where now it is only a source of loss.

The first form of wood waste to be encountered in studying the question is that of the tops, branches and roots, which are discarded in the bush. As a rule in this country, these are left to rot away where they fall, or else they are piled up and burnt to prevent further fire-risk, and to clear the ground for future growth. The logs themselves are usually floated to the mills and there the bark is stripped off and burnt, making another source of waste. These logs are then sawed up and another portion (ten to twenty per cent) goes to waste in sawdust, and still more wood goes into slabs and edgings, which are frequently burnt to dispose of them. Boards are cut to standard lengths and the odd ends are usually wasted. The defective pieces are frequently also burned. The shavings and odd pieces produced in planing mills generally go to waste and those made in actual construction work are practically always wasted. Most of these wastes are small in themselves and possibly many of them are too small even to be eliminated; but they are wastes nevertheless, and, as such, are responsible for some proportion of the high cost of living. It is only when they are taken in the aggregate that they assume proportions sufficiently great to make an impression on the ordinary layman. When, however, he is told that this waste amounts to \$10.00 or \$15.00 annually for every man, woman and child in the country, it begins to assume proportions such as may seem worthy of his notice.

How much of this waste it is possible to eliminate is, of course, unknown. A great deal of it is inevitable for the reason that the labor cost of putting many of these products into forms commercially valuable is greater than the value of the products so produced. But some of these can be utilized profitably, and one of the objects of the opening up of the Forest Products Laboratories is to discover and spread the knowledge of methods for such utilization.

Much has been done by the lumbermen themselves

*From Circular of Forestry Branch of the Department of Interior of Canada.

through their various associations to make an asset of many forms of waste wood. This work has been mostly along the lines of using up the small pieces produced by the mills which can be used to advantage by other mills, which do not necessarily require that their saw material be in large-sized sticks. Box factories, spool manufacturers, toy makers and factories making such articles as hammer-handles, etc., are frequently able to use the odd pieces produced in the manufacture of larger articles.

But the vast quantities of shavings, sawdust and edgings mostly go to waste yet and to these is directed the attention of chemists all over the world, since chemical utilization seems to be the most promising field in this connection.

The object of the following brief statements is to present a synopsis of some of the results already obtained, without going into the details of any of them. While all of these various industries have proved successful—that is, profitable—it should be recognized from the start that in each case much preliminary investigation is absolutely necessary, for what is successful in one locality may prove to be complete failure in another. Most of these industries require a large and constant supply of raw material, expert technical supervision, and frequently a considerable outlay of capital for expensive equipment. The market also has to be considered, particularly in its relation to the particular locality in which the raw material is found. When these conditions are found to be favorable after proper consideration, then it is well worth while going further into the matter.

Manufacture of Pulp and Paper.—The manufacture of pulp and paper from wood is an industry which has proved itself stable and of increasing magnitude for a number of years. Almost every kind of wood has been proved suitable for the manufacture of some form of paper, but there are considerations affecting the use of each kind which must always be observed. Most of the pulp is made from the wood cut specially for the purpose, but almost any wood can be used, provided that it is reasonably free from dirt, knots and bark, or that these can be easily removed from it. Sawdust is an exception to this rule on account of the fact that the fibers are cut so short that the pulp produced will not felt properly and the cooking is made considerably more difficult. There are several mills in the United States at present using mill-slabs, shavings and other forms of waste more or less entirely. The advantages of waste wood are, of course, its cheapness and its quantity. There are several disadvantages. It is usually green and full of water, has a large percentage of bark and comes in irregular shapes. Shavings are rather better for the purpose, and, if in sufficient quantity, make very good raw material. Another point to be taken care of in using waste material such as this is, to use the raw material of only one species, or, at least, species sufficiently alike that they may respond to the same treat-

ment. For instance, on account of the relatively large content of resin in longleaf pine, it will not do to treat this in the same way as spruce. Neither will it be satisfactory to work hard and soft woods together in any one treatment, though any of these can be worked satisfactorily if kept separate. The process to be used will depend chiefly on the raw material at hand and on the market for any particular variety of pulp.

Hardwood Distillation.—The distillation of hardwood, with the resultant production of charcoal, acetate of lime and wood alcohol, is an industry which is well developed and pretty stable. The latter two products are regularly quoted market articles. Charcoal is usually disposed of locally for domestic purposes, unless there is a charcoal-iron furnace within shipping distance.

Besides the wood cut especially for the purpose, hardwood slabs and other odd pieces of hardwood can be used. Where the wood is not cut especially for distillation, the plant is usually run in connection with a sawmill, so that only the part not suitable for lumber is used for the distillation. Almost any hardwood in pieces three or four inches in length and upward is suitable, but sawdust and shavings are not suitable—firstly, on account of the fact that the small size of the material makes it such a poor conductor of heat that it is impossible to char it completely in the ordinary forms of apparatus used, and, secondly, because the charcoal produced is so finely divided as to make it difficult to cool and handle, and because there is no market for it.

The woods most frequently used are beech, birch and maple, with smaller amounts of other woods as they may occur with the first-mentioned.

Resinous Wood Distillation.—The development of the industry of distillation of resinous, or "soft" woods for the production of charcoal, wood creosote and turpentine, is much later than that of distilling the hardwoods, and the practice is not yet standardized to any great extent, though a great deal has been done along this line in the last few years. The value of a resinous wood for distillation is in proportion to the amount of resin, or "pitch," contained in the wood. The resin content is quite variable, even in trees of the same species and in different parts of the same tree, so that some care is necessary in the selection of the wood for distillation to avoid using wood which is too lean to yield a profit.

Pine is the wood most used and is taken mostly in the form of "lightwood." Stump-wood is also used to a considerable extent, but is usually left to the last, since it is much harder to collect and handle. Almost any kind of resinous wood is suitable to some extent, the only question being whether it contains sufficient resin to make the recovery worth while, and so is largely a matter to be considered in connection with the particular location in question. Where sawmill waste is used, the matter of selection is not so important, as the cheapness of this material makes up, to

some extent, for the poorer material. This class of material, however, is not rich enough to render the more complex and expensive processes feasible, and the simpler and more rapid steam-distillation processes must be used. This recovers only the volatile oils which were originally present in the wood, and so the process is very wasteful, but is the only one at all successful with this class of material. Destructive distillation plants for resinous wood are the cheapest form to construct. They produce products of rather poor quality, however, and so the market is somewhat restricted. There are also some processes known as "bath processes" in operation. In these the wood is run into a retort and flooded with some high-boiling solvent of the turpentine and light oils. These are heated and extract the oils from the wood, and are then drained off and the oils recovered from the solvent by distillation with steam. Various solvents are used, but rosin appears to be the best at present.

Processes using a low-boiling solvent, such as naphtha, have found increasing use in the last few years, but the decreasing price of turpentine and the increasing cost of solvent has made the business increasingly difficult.

Tanbark and Tanning Extract.—Tannin is obtained from the leaves, bark and wood of a great many trees, but only a few of these (practically only hemlock and a couple of species of oak) are used commercially. Usually these are sold in the form of bark and the tanners make the extract themselves. In some cases, however, it may be of advantage to make the extract nearer the bush and save the freight on the bulky bark. The method of extraction is very simple and the extract can easily be concentrated and shipment made easy.

Manufacture of Ethyl Alcohol.—This is a process for the manufacture of ethyl (or "grain") alcohol from wood as distinct from the methyl (or "wood") alcohol produced by the destructive distillation. Ethyl alcohol is not poisonous in the same way as wood alcohol, and a very broad market is open for it, if production is made sufficiently cheap. Since the wood used in this process must necessarily be finely divided, almost any kind of waste wood is suitable as the large-sized pieces can be easily reduced to the proper size.

The process used consists of the conversion of the cellulose of the wood into a sugar; the sugar is then fermented to produce the alcohol and this is distilled off. The process is on a paying basis in Europe, and in at least one plant in America.

Cattle Food.—Cellulose, or wood fiber, may be converted—at least partially—into a sugar, with comparative ease. There are also several other carbohydrates formed in the process. A considerable proportion of the products so made are digestible by cattle, and, especially when mixed with other products, such as peanut meal, rice meal, alfalfa, it seems to make good cattle food and finds a market.

Manufacture of Oxalic Acid.—Finely ground wood

fused with caustic soda forms sodium oxalate from which oxalic acid may easily be produced. The manufacture of this product may prove profitable, though the restricted market would be against it. A very little wood used in this way would produce all the oxalic acid used in the country. Almost any species of wood is suitable.

Waste Wood for Producer Gas.—Several forms of apparatus for the production of producer gas from waste wood have been put on the market lately and are finding considerable favor. The production of power from waste wood in this way is much more economical than burning the wood under steam boilers, especially when small-sized stuff, such as sawdust and shavings, are to be disposed of. The commercial success depends on the demand for the power produced. Any kind of wood can be used, though it is an advantage to have it of fairly uniform size and preferably dry. The woods with the higher calorific values are, of course, somewhat more efficient.

Further information regarding any of these methods will be gladly supplied by the Forest Products Laboratories, McGill University, Montreal.

The work of these laboratories is directed entirely along the lines of utilization of wood waste and improved methods in the manufacture of forest products.

All information and results of the laboratories are free to the public and will be gladly supplied upon request.

RECENT IMPROVEMENTS IN GAS MANUFACTURE.*

By ALFRED E. FORSTALL.

The process of manufacturing illuminating gas divides itself into two stages, the generation of crude gas from the raw materials, and the purification of this crude gas to make it fit for general use.

Taking up first the generation of coal gas, an important recent improvement is the development and quite general installation of retorts set vertically, which was unsuccessfully tried in the early years of the nineteenth century. Retorts set horizontally have been used solely, until, in 1885, M. Andre Coze developed a setting in which the retorts were inclined at an angle of from 29° to 33° to the horizontal. At such angles the coal would spread fairly evenly over the whole length of the retort by gravitation and the coke would run out fairly easily when the charges were thoroughly carbonized. Though adopted quite generally abroad, only three important installations of inclined retorts, and not more than five or six minor ones, were made in the United States.

In the year 1902 two types of vertical retort settings, the intermittent and the continuous, were brought to the attention of gas men. The intermittent type, in

*From a paper read before the New York Section of the Society of Chemical Industry, and reprinted in the American Gas Light Journal.

which a quantity of coal which nearly or entirely fills the retort is put in at one time and allowed to remain until the whole is carbonized when the resulting coke is dropped out, also at one operation, was developed by Dr. Bueb in the gas works at Dessau, Germany. The first patent taken out on these retorts, in 1902, described them as provided with outlets, spaced from top to bottom along the length of the retort and opening into a vertical flue so placed in the setting as not to be exposed to a high heat, the object being to permit the gas driven out of the coal to escape to the hydraulic main without being subjected to contact with either the highly heated coke or the walls of the retort. Settings built under this patent were put into operation in 1903 but the side outlets were abandoned soon after actual operation began, and by 1905 the design had been developed to that which is now employed, in which the gas evolved from each portion of the charge travels through all the superincumbent portion, before it escapes to the hydraulic main.

In the Dessau verticals as developed in Europe the retorts are made either four meters or five meters (13 ft. 2 in. or 16 ft. 5 ins.) long with cross-sectional dimensions of approximately 9 ins. by 22 ins. at the top and 14 ins. by 27 ins. at the bottom; and are set in groups of 12 or 18, each group heated by its own gas producer, or generator furnace, and provided with its own recuperators. In the only installation of this type in the United States (Providence, R. I.) the retorts are 13 ft. 2 ins. long with the cross-section given above and are set ten in a bench. The coal is charged into the retorts from overhead bunkers and the coke is dropped into buggies or a conveyor.

The combustion of the producer gas takes place in a combustion chamber surrounding the lower ends of the retorts; and the products of combustion pass horizontally to the back of the setting and then up to a second set of horizontal flues running to the front, up again to a third set running to the back and then into a fourth set running to the front and pass out from top of the bench to the recuperators and thence to the chimney.

Intermittent Vertical Retorts—U. G. I. Co.—In America the United Gas Improvement Company began experimenting with intermittently filled vertical retorts about 1908. The benches of this type last built contain nine retorts each 18 ft. 6 ins. long with an oval section 12 ins. by 22 ins. at the top and 18 ins. by 30 ins. at the bottom. The reasons for the larger cross-section are that when smaller the coal coked too rapidly at the top of the retort, causing excessive pressure at the bottom, that with the small retort the discharge of the coke did not take place satisfactorily except when the whole charge of coal was thoroughly carbonized, while a large retort will discharge readily even when the coal has not been thoroughly carbonized, and that the larger retorts produce larger coke, an advantage in many localities. In this setting the production of the producer gas also takes place around

the lower ends of the retorts and the products of combustion pass upward to the top of the setting.

The German practice is to fill the retorts completely with coal while the United Gas Improvement Co. leave 4 ft. of the retort at the top empty, to provide a space in which the heavy hydrocarbon vapors may be converted into gas by the action of radiant heat.

It is interesting to note that in 1880 Mr. C. F. Dietrich obtained a United States patent making claims for a setting of retorts which were very similar to those of the original Bueb patent, including even the lateral openings into a channel protected from heat through which the gas could pass from the retort. At that time, however, conditions in this country were favorable to the manufacture of carbureted water gas and the field for coal gas did not seem to warrant the trouble of developing a new method of manufacture, so that apart from building one experimental bench nothing was done to develop these retorts.

Passage of Gas Through Intermittent Retorts.—The reason for the side outlets in the retorts under the original Bueb patent was the belief that, if compelled to pass up through the incandescent charge, the hydrocarbons first evolved from the coal would be decomposed into hydrocarbons of lesser illuminating and calorific value; and that carbon and naphthalene would be formed and cause trouble in handling the gas as it passed from the generating apparatus to the consumer. The disadvantage of the side outlets was that the retort could not be heated around its entire perimeter and that, therefore, more fuel was required for the carbonization of a given weight of coal. When the lateral outlets were bricked up and the gas taken off at the top of the retort the decomposition of the hydrocarbons was not as great as had been anticipated, provided the retorts were heated to a very high temperature and care taken to completely fill them with coal. It was claimed that under these conditions the generation of the gas from the portions of the coal was at once converted into a compact coke, impermeable to the gas generated. The gas was therefore forced to pass, from all points of the layer in which carbonization was taking place inward and upward through the uncoked and more permeable central portions of the charge. Its temperature was thus prevented from rising to the point at which over-decomposition of the heavy hydrocarbons, with the formation of carbon and naphthalene, would take place.

This theory as to the course taken by the gas in passing through the charge in an intermittently charged vertical retort was for a long time accepted as correct, but recently Dr. H. L. Colman, in England, and Mr. O. B. Evans, in the United States, have reached the conclusion, as the result of experiments, that in reality only part of the gas travels through the core of uncarbonized coal and the rest travels through the incandescent coke. Dr. Colman argues that if even the largest portion of it traveled through the uncarbonized coal, the gas would show some of the charac-

teristics of a gas produced at a low temperature, modified to some extent by the gas produced in the latter stages as the temperature of the coke is raised, and that the tar produced would be a low temperature tar containing but a small amount of aromatic substances. As a matter of fact, his analyses show that the gas possessed all the characteristics arising from exposure to high temperatures, the proportion of hydrogen to methane being even higher than that obtained from the same coal distilled in highly heated horizontal retorts, and the tar produced, although containing more paraffin derivatives than tar from horizontal retorts, consisted chiefly of aromatic substances, showing that, during its formation, the vapors produced at low temperatures must have been subjected to a considerably higher temperature before passing out of the retort. This could not happen if even the larger part of the vapors passed through the uncarbonized coal, since the travel would be in a direction that would expose them to a constantly decreasing, instead of a higher temperature. Moreover, the existence of a high pressure in the retort at the commencement of carbonization when the area of the core was greatest, and the diminishing of this pressure as carbonization proceeded, although the rate at which gas was produced did not decrease greatly during the first seven hours, while the area of the core did decrease quite rapidly, was strong evidence that the gas did not find its principal exit through the core. He concludes that the great bulk of the gas is produced on the outer side of the pasty layer formed by the coal as it carbonizes, and that the gas travels mainly through the hot coke, mixing with the poorer gas produced by the continued action of heat on the low-temperature coke first made. The gas produced in the inner side of the pasty layer will pass through the coal and he considers it probable that the vapors which pass in this direction form the undesirable paraffin constituents of the tar so that as far as travel through the core does take place it is disadvantageous.

Mr. Evans, reasoning from the pressure conditions existing in the interior of an intermittently charged vertical retort, came to the conclusion that during the early part of the charge, when the layer of coke formed around the perimeter of the retort was compact and offered no ready means of passage to the gas, most of the gas produced was obliged to force its way through the pasty layer of coal in the initial stage of carbonization, and pass up through the uncarbonized coal, but that as the outer layer of coke contracted and cracked under further heating most of the gas formed in the latter portions of the charge passed up through this coke. He also concluded that of the gas made during the first 6 hours, which amounted to 70 per cent of the total made, 45 per cent passed up inside of the pasty layer through the core, and 55 per cent through the hot coke next to the retort walls, and that the gas evolved at low temperatures escapes through the core while that evolved at high tempera-

tures escapes along the wall. Mr. Evans considers that this is advantageous since the low temperature gas is more subject to injury by exposure to heat, and this is correct provided that after leaving the coal this gas is exposed to heat in a free space at the top of the retort. This discussion as to the path followed by the gas in passing out from intermittently charged vertical retorts has been given somewhat at length because of the claims originally made that the freedom from naphthalene experienced with gas made in such retorts was largely due to the fact that the travel was through the cool core of uncarbonized coal.

English Development of Continuous Vertical Retorts.—While the work of the Germans with vertical retorts was confined to those charged intermittently, in England the design was approached with the idea of adapting them to continuous carbonization. This had been tried with horizontal retorts and had given good results as far as the quantity and quality of the gas were concerned but had failed because of mechanical troubles. In 1902 a setting of vertical retorts was built at Exeter, into which the coal, in amounts varying from 2 lbs. to 7 lbs. was charged at regular intervals, the length of which could be varied. The retorts, about 9 ft. long, were made straight for part of the distance and then curved so that the coke was withdrawn through an opening in the side of the setting. The coke was drawn intermittently in comparatively large quantities at a time so that the extent to which the retort was filled with coke and coal varied considerably. After being tried in other places in England, further use of the settings was abandoned because of trouble with the coal-feeding device and in keeping the curved portion of the retort from cracking, and also with the formation of lampblack owing to the large variation in the volume of the charge because of the intermittent drawing of the coke and the consequent variation in the extent to which the gas passing off from the charge was exposed to heat in the vacant space at the top of the retort.

Woodall-Duckham Vertical Retorts.—While this retort was being experimented with, Messrs. Woodall and Duckham were developing at Bournemouth, another type of continuously charged verticals, starting with a mechanical coal feed and mechanical continuous extraction of the coke. The first was soon abandoned because of operating difficulties and the introduction of coal into the retort is now brought about entirely as a result of the extraction of coke from the bottom. As now built, each retort is surmounted by a charging magazine filled through a rotary valve from an overhead coal bunker and holding enough coal for 2 hours' supply. There is free communication between the magazine and the top of the retort, the coal in the former being supported by that in the retort. As the extractor withdraws the coke from the bottom the whole column of material in the retort settles and coal runs in at the top from the magazine, which is re-

plenished with coal at intervals of from 20 minutes to an hour.

The coke extracting device consists of a rotating horizontal shaft provided with arms placed spirally around it, and of loose arms hung on hinges at their upper end and having sufficient weight to hold back the coke except as their lower ends are pushed out by the action of the revolving shaft. The coke is discharged into a closed hopper which will hold the amount produced during 2 hours, and is intermittently emptied either into dumping wagons or into a conveyor. The extractor can be run at varying speeds to suit the quantity of coal that can be carbonized under varying conditions.

As originally built, the settings consisted of four oval retorts 25 ft. long and having cross-sectional dimensions of practically 9 ins. by 23 ins. at the top and 20 ins. by 29 ins. at the bottom. In recent installations the retorts have been replaced by rectangular ovens, or slots, of the same length and having cross-sectional dimensions of 8 ins. by 3 ft. 10 ins. at the top and 20 ins. by 5 ft. 3 ins. at the bottom. At the top of these slots there is a division plate, extending down on adjustable distance, forming two separate spaces, into one of which the coal magazine opens while the other is kept free from coal so that the gas can pass out through it and in passing out be exposed to radiant heat for the purpose of decomposing the hydrocarbon vapors with low boiling points. As the settings are operated it would seem that the desired effect is obtained to only a very limited extent, if at all. The combustion of the producer gas begins at the top of the setting and the products of combustion pass down, surrounding the retorts and are taken off into the recuperators a short distance above the bottom. From the recuperators they pass either directly to the chimney or in some cases through a waste heat boiler which furnishes the steam required for the operation of the plant. The primary air is heated before entering the furnace by passing across the setting in contact with the side walls of the retorts at either lower end, and the coke is sufficiently cooled in this way to require no quenching.

Glover-West Vertical Retorts.—During this time Messrs. Young and Glover at St. Helens were working what is now known as the Glover-West system of continuous vertical retorts. The chief differences between the Woodall-Duckham and the Glover-West systems are in the form of the coke extractor and in the methods of heating the retorts. In both, the coal runs into the retorts from a charging magazine as the coke is extracted at the bottom. The coke extractor with Glover-West is a worm with its axis vertical which slowly revolves and delivers coke into a receiving chamber, large enough to hold that produced during 2 hours and regularly discharged at any interval of less than 2 hours. The retorts are oval in section and have a total length of 20 ft. with cross-sectional dimensions of 10 ins. by 30 ins. at the top and 22 ins.

by 36 ins. at the bottom. To the bottom of each one is added a cast iron chamber 3 ft. deep, at the bottom of which is placed the coke extractor. The retorts are set in groups of eight, and the setting divided into either two or four chambers so that the retorts can be worked in units of four or two. The combustion of the producer gas takes place at six points evenly spaced along the portion of each chamber extending from the bottom to within about 5 ft. of the top, and the products of combustion, after passing horizontally around each set of retorts, ascend through vertical flues to chambers surrounding the upper 5 ft. of the retorts, from which they pass to the chimney. The secondary air is heated by passing the cast iron chambers at the lower end of the retorts and this cools the hot coke on its way to the coke extractors, and does away with the necessity of quenching it when taken from the coke chambers.

Operation of Horizontal Retorts Modified.—Partly as a consequence of the successful introduction of intermittently charged vertical retorts the method of operating horizontal retorts has been substantially modified. This had been to charge such retorts with a layer of coal about 4 ins. to 5 ins. thick leaving a large free space above the coal, through which the gas passes to the mouthpiece and standpipe. The maximum charge for a 9-ft. retort with one end permanently closed, in general use in the United States, was from 340 to 350 lbs. of coal. The front end of the retort being enclosed in the wall of the bench for a depth of 13 ins., a foot of the length was not effective for carbonizing purposes and the weight of charge was not more than 45 lbs., and in many cases 40 lbs. per lineal foot of the effective portion. There had been some theoretical discussion of the advisability of more completely filling the retorts, but this had not produced any result in practice until the completely filled vertical retorts afforded an object lesson of the freedom from carbon and naphthalene troubles secured by reducing the contact of the gas with the highly heated walls of a retort. In England, where the use of retorts open at both ends was common, it was easy to change from lighter charges to heavier ones, but in the United States it was necessary to change to through retorts instead of single end ones before the increase in weight of charge could be made, since where the coke is drawn from the retort by a rake it is necessary to leave sufficient space above the charge to permit the free passage of the rake; while from through retorts the coke can be pushed and provision for the passage of the rake does not have to be made. The present practice, with through retorts, is to charge about 70 lbs. of coal per lineal foot of the effective portion of the retort. When so charged from 60 per cent to 70 per cent of the area of the retort is occupied by coal, leaving only 30 per cent to 34 per cent of the area for the passage of the gas; while a 40-lb. to 45-lb. charge only occupies from 30 per cent to 36 per cent of the area. The expansion of the charge dur-

ing the coking process makes the actual free space left in the retort still smaller in proportion for the heavy charges. The use of heavier charges has resulted in a large increase in gas made per pound of coal, with a decrease of those operating difficulties caused by free carbon in the gas and in the tar. In England the yield of gas formerly averaging about 10,500 cu. ft. per ton of 2,240 lbs. of coal now averages nearly 12,000 cu. ft.; while at Worcester, Mass., the former average yield of 5 cu. ft. per pound has been increased to 5.9 cu. ft. Other works in the United States which have adopted heavy charges have increased the yields of gas about 10 per cent without any decrease in illuminating value or calorific value per cubic foot; therefore obtaining greater total illuminating value and calorific value in the gas from a given quantity of coal.

The yield from continuous vertical retorts is also greater than that formerly obtained from horizontal retorts operated with light charges, but in this country is not as large as that obtained from the horizontal retorts at Worcester, Mass.

Comparison of Gases from Horizontal and Vertical Retorts.—These analyses are of the gas made in two plants, one having horizontal retorts and the other vertical retorts of the Woodall-Duckham type. The horizontal retorts are operated with moderately heavy charges not, however, up to 70 lbs. per lineal foot of retort. These plants are under one management, and the coal is purchased from one company and is presumably the same, so that the analyses show, to some extent, the differences due to the methods of carbonization. The total illuminants run slightly higher, and there is much less hydrogen in proportion to the methane, in the gas from the vertical retorts. The illuminating value of the gas from the verticals is higher, while the yield per pound of coal is 10 per cent greater. In the horizontal retorts very wet coal was being carbonized and this may have affected the illuminating value and the yield of gas which were lower during this period than the average for the preceding month; but even the averages for that month were lower than the results obtained from the vertical retorts which were those made during a test lasting 8 days, and in regular working the results have not been quite as good.

	Horizontal retorts. Per cent.	Vertical retorts. Per cent.
Carbon dioxide	1.44	1.49
Benzol	0.67	0.55
Illuminants	3.15	3.98
Oxygen	0.48	0.28
Carbon monoxide	4.75	6.90
Hydrogen	51.36	45.02
Methane	33.60	37.33
Nitrogen	4.55	4.44
	100.00	99.99
Candle power (Sugg D burner)	13.60	15.57
Calorific value (B.T.U. per cubic feet by calculation)	610.00	
Calorific value (B.T.U. per cubic feet observed)		615.00
Yield, cubic feet per pound of coal	4.85	5.39

Comparable analyses of the gas made in the working scale testing plant at the gas works in Birmingham, England, in intermittent vertical retorts of the Dessau type apparently charged so as to leave a free space above the coal at the top of the retort, and in horizontal retorts are given by Dr. W. B. Davidson, as follows:

	Dessau verticals. Per cent.	Hori- zontals. Per cent.
CO ₂	2.4	2.2
C ₆ H ₆	2.8	3.4
O ₂	0.5	0.5
CO	10.3	9.7
CH ₄	28.0	31.5
H ₂	51.0	47.3
N ₂	5.0	5.4
	100.0	100.0
Illuminating value, candles	15.0	18.0
Net calorific B.T.U. per cubic feet	500.0	525.0

Note.—The illuminating values given by Dr. Davidson cannot be compared directly with those given previously since they were obtained on the Metropolitan No. 2 Argand burner and are probably about three candles higher than would have been obtained with the Sugg D Argand used in the other case.

Dr. Davidson observes that the gas made in the vertical retort is deficient in unsaturated hydrocarbons and methane, and high in hydrogen, and that a cursory examination of the analyses leads to the conclusion that the hydrocarbon gases are subject to more drastic degradation before leaving the retort in the vertical system than they are in the horizontal system, but that it is not unlikely that the gas suffers both in quality and volume by the escape uncracked of a larger proportion than usual of tar oil vapors. Experience with the United Gas Improvement Company verticals operated with a large free space above the coal seems to show that this space leads to an improvement in the illuminating and calorific value of the gas, which is obtained at the expense of the extra quantity of tar produced when the retorts are completely filled.

In quality and quantity of gas intermittent vertical retorts of the Dessau system give poorer results than are obtained in horizontal retorts, while the intermittent verticals of the United Gas Improvement Company type, and continuous verticals do not give any better results than can be obtained from properly operated horizontal retorts. The improvements effected by vertical retorts consist in a saving of labor in medium-sized plants in which it is impossible to work charging and discharging machinery for horizontal retorts to advantage, and in greater freedom from trouble by free carbon and naphthalene; while the sulphur compounds other than sulphureted hydrogen are also produced in smaller amount. In addition there is a saving in ground space required, although it is necessary to go higher into the air with verticals. To these advantages the continuous vertical retort system adds that of practically complete avoidance of the smoke and steam emitted during the charging and discharging of horizontal retorts and intermittent vertical ones.

Suggested Method of Distillation.—The character of the products given off by coal subjected to distilla-

tion at different temperatures indicates that the greatest gas making efficiency would be obtained by so adjusting the heating of continuous vertical retorts that the temperature of the upper 2 or 3 ft. of the charge would never exceed $1,000^{\circ}$ to $1,100^{\circ}$ F., while the lower portion of the charge was carried as high as $1,800^{\circ}$ F. By this method of heating, the rich hydrocarbons would be driven off without having to come into contact with very highly heated surfaces, while the remaining gas, which is of such a character as not to suffer to any great extent from each contact, would be expelled from the coal when in the lower portion of the retort.

To decompose the heavy hydrocarbon vapors (which would otherwise condense into tar), and to convert them into the maximum amount of permanent gas mixed with hydrocarbon vapors that could be carried by the gas, all of the gas leaving the top of the charge should be passed through a free space exposed to heat radiated from walls at a temperature adjusted to the rate of travel of the gas, but probably about $1,400^{\circ}$ to $1,500^{\circ}$ F. This space could be maintained either in the upper part of the retort or, if this leads to difficulty in feeding the coal, it might be entirely separate from the retort and possibly common to several retorts. This method of manufacture would increase the quantity and quality of the gas at the expense of the tar, and would not be advantageous unless the value of the gas gained was greater than that of the tar lost. It has never been actually worked, but in my opinion is entirely feasible.

Improvements in Manufacture of Carbureted Water Gas.—Recent improvements in the manufacture of carbureted water gas consist in the general use of appliances for measuring the air blown through the fuel bed during the "blow," and the steam passed through the fire during the "run," and the use of the electric pyrometers for indicating the temperatures existing at selected points in the checker brick of the carbureter and superheater. These appliances make it possible to constantly operate the apparatus under those conditions of blast, steam and temperature that will give the best results; and by so doing decrease the fuel used and increase the efficiency of the conversion of the oil into oil gas.

Preparation of Crude Gas for Delivery to Consumer.—In the second division of the process of gas manufacture, that of the preparation of the crude gas for delivery to the consumer, the recent improvements have been chiefly in connection with the removal of hydrogen sulphide and the other sulphur compounds present in the crude gas. For many years attempts have been made to use the ammonia obtained from the gas for the removal of hydrogen sulphide from coal gas. About 1886 a process for doing this was devised by Claus in Belfast, Ireland. Although chemically correct, it proved too complicated mechanically and was finally abandoned. It is possible that if modern centrifugal pumps had been available the

process might have been successfully operated. In the United States an extremely simple method has been recently devised by Mr. Jas. G. O'Neill and used on coke oven gas sold for illuminating.

The ammonia in ordinary ammoniacal liquor is already largely saturated with sulphur and carbon dioxide and one of the chief problems in connection with the use of this liquor for more complete removal of sulphureted hydrogen is to accomplish its conversion into a condition suitable for combination with sulphureted hydrogen without introducing too much complication of apparatus. Mr. O'Neill has solved this problem by using liquor withdrawn from a still of the Coffey type, which is in general use for the concentration of ammoniacal liquor. He finds that when the liquor fed to the still has reached the point at which it has a temperature of 214° to 215° F. it has lost 80 to 90 per cent of the hydrogen sulphide, and 70 to 80 per cent of the carbon dioxide, but still retains practically all the ammonia it contained when it entered the still. When brought in contact with crude coal gas in scrubbers of the ordinary type, this liquor will take up on an average 500 grains of hydrogen sulphide per gallon and if used in sufficient quantities will reduce it from as much as 900 grains, down to from 20 to 30 grains, per cubic foot of gas. If the complete removal of the hydrogen sulphide with liquor is attempted the efficiency of the liquor is much less than this and it is much more economical to use the liquor only to the extent named and then finish the removal by hydrated sesquioxide of iron.

Mr. O'Neill's process adds to the apparatus customarily found in gas works only a heat exchanger, in which heat is transferred from the hot liquor coming from the concentrating still to the cool liquor on its way to the still, and a cooler for further cooling the treated liquor, both of which are inexpensive. Apparently this process could be adopted in many coal gas works with a saving in labor required to operate the oxide of iron purifiers, and in the investment in the purifiers required for a given quantity of gas.

Removal of Other Sulphur Compounds.—In Europe, where the gas coals contain, as a rule, more sulphur than those in common use in the United States, and on the Pacific Coast, where gas is largely made from crude petroleum containing a high percentage of sulphur, the problem of reducing the sulphur compounds, other than hydrogen sulphide in crude illuminating gas, has had some importance. Therefore, attention has recently been paid to new methods of removing the principal one of these sulphur compounds, carbon bisulphide. Of the recent processes, the one first brought to the attention of gas engineers was that devised by Messrs. Hall and Papst and used since 1908 for the treatment of all the gas made (about 3,000,000 cubic feet per day) at Portland, Ore. In this process the gas is heated to from $1,300^{\circ}$ to $1,600^{\circ}$ F. by being passed through tall cylindrical vessels filled with checker work of fire brick, which are

heated by the combustion in them of fuel oil. The vessels are in pairs, one being in process of heating while gas is being passed through the other. The operations are reversed as soon as the vessels through which the gas is passing becomes cooled below the effective temperature. Under the effect of heat the carbon bisulphide reacts with the water vapor present in the gas and is largely converted into hydrogen sulphide, which is removed by purifiers containing oxide of iron.

Nickel Catalyzer for Decomposition of Carbon Bisulphide.—Another process employed on a large scale is that devised by Mr. E. V. Evans and used to treat the gas made (about 10,000,000 cubic feet per day) at the works of the South Metropolitan Gas Company, London. This process utilizes the catalytic effect of nickel in accelerating the reaction between carbon bisulphide and steam, by which hydrogen sulphide is produced and carbon set free. The catalyzer is in the form of balls of fire clay, one inch in diameter, impregnated with nickel obtained by the reduction of the chloride in a current of hydrogen. These balls are contained in tubes 11.5 feet long, and of 6-in. diameter, through which the gas is passed. Before reaching the catalyzing tubes the gas passes through heat exchangers, or recuperators, in which it absorbs heat from the gas passing out from the apparatus, and then through preheating tubes in which its temperature is raised to 750° F. With this preheating of the gas it is possible to carry on the process at a temperature of 800° F. in the catalyzing tubes. A single combustion chamber, supplied with producer gas from an outside producer, furnishes the heat for both the preheating and the catalyzing tubes. After about thirty days' use it is necessary to stop the flow of gas through a set of catalyzers and blow air through them to burn off the deposited carbon which is found to be, at times, 50 per cent in excess of the quantity calculated from the amount of carbon bisulphide reduced to hydrogen sulphide. This carbon may come from the decomposition of hydrocarbons in gas, but analyses of the gas before and after treatment, which are given below, show that the quantity so decomposed is negligible.

	Gas before treatment. Per cent.	Gas after treatment. Per cent.
CO ₂	1.82	1.80
C ₂ H ₄	3.61	3.79
O ₂	0.27	0.07
CO	8.85	8.62
CH ₄	26.62	27.45
H ₂	52.45	52.19
N ₂ (by difference).....	6.38	6.38
	100.00	100.00
Illuminating power in English candles...	14.05	14.05
Calorific value, B.T.U. per cubic feet...	590.00	594.00

Soda-Cellulose for Removal of Carbon Bisulphide.—Another process tried at an experimental plant of the Heidelberg, Germany, Gas Works consists in treating the gas, entirely freed from tar, ammonia, sulphureted hydrogen and carbon dioxide, with a compound of soda and cellulose obtained by treating

cellulose sulphite with soda lye. The resulting material rolled and crumbled to a powder, is placed on trays in purifying vessels in the same way as oxide of iron. When brought into contact with carbon bisulphide the soda cellulose is changed into cellulose xanthogenate or viscose, the raw material from which are obtained cellulose hydrate and the formyl-cellulose used in the manufacture of non-inflammable celluloid. In the experimental plant ten tons of the soda cellulose material, known as "athion," absorbed 1.25 tons of carbon bisulphide, so that with gas containing 45 grains per 100 cubic feet, ten tons would purify over 35,000,000 cubic feet of gas, but the cost of operation is not given. Since it is not the custom in the United States to remove carbon dioxide from illuminating gas, the employment of this process would involve the installation of additional apparatus for that purpose.

Oxide of Iron Catalyzer for Decomposition of Carbon Bisulphide.—A very promising process, not yet tried on a working scale, is based upon the fact that at temperatures above 100° F. metallic iron acts as a catalyzer in the reaction between bisulphide of carbon and moisture in illuminating gas. The fact that gas, free from sulphureted hydrogen, contained this substance after having passed through a wrought iron service pipe running near a steam pipe, attracted the attention of Mr. J. G. Taplay, and experiments made by him showed that at a temperature of 158° F. the reaction between the bisulphide of carbon and moisture with the formation of sulphureted hydrogen took place quite rapidly, in gas traveling through a wrought iron pipe, and also that as the interior of the pipe became rusted the sulphureted hydrogen produced was absorbed by the oxide of iron and did not show at the outlet of the pipe. A French gas engineer, M. Guillet, observed the same action taking place inside a gas holder and by experiments determined that when gas containing bisulphide of carbon was passed through ordinary oxide of iron purifying material at temperatures above 25° C. (72° F.) 25 per cent of the original content of carbon bisulphide was removed. He found 100° C. (212° F.) to be the temperature at which the change became interestingly rapid, while at a temperature of 130° C. (266° F.) more than 67 per cent of the bisulphide originally present was converted into hydrogen sulphide and removed. The percentage removed increased with the amount originally present, the treated gas containing only from 3.01 to 5.82 grains, while the original gas contained from 9.48 to 24.42 grains of bisulphide per 100 cubic feet.

Since the efficiency of oxide of iron for the removal of sulphureted hydrogen is very much increased by heating and it should not be difficult to maintain the temperature of the purifying material at the comparatively low temperature of, say, 250° F., this process would seem to offer the simplest and most inexpensive means of removing from illuminating gas the larger part of the bisulphide of carbon which it con-

tains after the treatment ordinarily given to it in gas works, whenever the amount of this impurity present is sufficiently large to make it important that it should be reduced.

DRY-MILK INDUSTRY OF NORWAY.*

The dry-milk industry of Norway is passing through a transitional stage that has temporarily caused an almost complete cessation of manufacture, there being only one plant now in operation. The industry is readjusting itself to new processes, since the methods previously used have been found unsatisfactory. The plant now running uses the so-called chemical spraying process, but other factories being planned contemplate the use of purely mechanical processes, which it is said have the great advantage of producing a milk meal possessed of practically unlimited keeping quality. In recent years competition from Holland, Germany, France, and other countries has caused a demand for better qualities of milk meal than the earlier system could produce.

There are two evaporated-milk factories near Stavanger, equipped with English machinery, but operations ceased about a year ago. The manager of these plants now announces that he will shortly reopen one of the factories.

Development in Methods of Manufacture.—The first dry-milk factory in Norway was started in 1902, the machinery installed being of Swedish make and based on the vacuum principle. About 1904 this process was sold to an American company, which has improved it and is now successfully using it; the system as originally used was too limited in the capacity of its machinery, and the supplementary drying processes necessary to perfect the product did not give very satisfactory results. The milk meal made from this process was insoluble—i. e., not soluble in pure water—which is said to be no serious drawback, because most of the uses to which the dry milk is put do not require solubility; keeping quality is more essential, especially if it must be transported any distance.

American machinery introduced in 1908, employed a pressure of 3 atmospheres (45 lbs.), and the product is said to have been quite satisfactory, although the casein became rather hard. English machinery was introduced in 1911, being of the same general cylinder type as the American, but with the notable difference of a greatly reduced pressure, made possible by utilizing condensing valves.

Invention of a New Process.—A Stavanger capitalist, interested as a manufacturer of dry milk since the inception of this industry in Norway, has invented a process which is now being tested and will later be utilized in larger plants. Patents have been taken out in most countries, including the United States. The process is entirely mechanical and is in no way based on previous vacuum, pressure, or spray systems. The

apparatus consists of a drying chamber built of bricks, insulated wood, and metal lining, within which is passed an endless traveling steel band about 20 ins. in width. Through the top of the drying chamber a vessel is inserted, wherein the milk is vaporized before supplying it to the band for final drying. In this vessel the vaporization rids the milk of two-thirds to three-fourths of its original content of water.

A revolving cylinder, dipping into a cup of the partly vaporized milk, conveys the liquid to the slowly moving metal band, the milk film being thus passed into the drying chamber where it is subjected to superheated circulating air, and when scraped off from the band by a keen-edged knife contains only 2 to 5 per cent of water. The degree of desiccation may be regulated by controlling the temperature of the heated air, and, to some extent, by varying the velocity of the steel band.

There are many other details of the process claimed to be new to the industry. The machinery can also be utilized to advantage by dairies as a subsidiary industry, as separated milk thus becomes a profitable by-product in being immediately converted into milk meal.

Analysis and Uses of Dry Milk.—Dry milk, sometimes called evaporated milk or milk meal, must not be confused with condensed milk, for the two have quite different analyses and are produced by entirely different processes. A quantitative analysis of dry milk made in Stavanger from the new process showed that the three grades of the product contained the following constituents:

Kind of milk used.	Water. Per cent.	Fat. Per cent.	Casein. Per cent.	Sugar. Per cent.	Mineral Per cent.
Full cream.....	3.70	28.78	25.95	34.64	5.43
Part cream.....	4.96	16.06	29.00	42.63	5.75
Separated	5.28	.34	30.30	55.30	7.75

Dry milk is useful chiefly in connection with products of the bakery, being employed to good advantage as an ingredient in ice cream, bread, biscuits, and chocolate. It is coming to be used more and more on ships, expeditions, and explorations, where convenience of transportation and keeping qualities are prime considerations. Roald Amundsen, the discoverer of the South Pole, has included Norwegian dry milk as an essential part of the ration equipment on his polar expeditions. Several tons of it have recently been manufactured in Stavanger for the use of his party during his forthcoming North Pole expedition.

The quantity of fluorspar mined in the United States in 1913 was 115,580 short tons, valued at \$736,286, compared with 116,545 short tons, valued at \$769,163, in 1912. The average price per ton for the whole country, considering all grades of fluorspar—gravel, lump, and ground—was approximately \$6.37 a ton in 1913, compared with \$6.60 in 1912. Fluorspar was produced in 1913 in six states—Illinois, Kentucky, New Mexico, Colorado, New Hampshire, and Arizona—in the order named.

*From Daily Consular and Trade Reports.

GRAPHITE TRADE AND PRODUCTION.

The following notes on the production and trade in graphite are taken from a recent issue of the Daily Consular Trade Reports:

GERMANY.

The kingdom of Bavaria is scantily supplied with minerals and for many years the graphite deposits in the vicinity of Passau were deemed of little value. More recent investigations, however, indicate not only that these may be a source of great wealth to the country, but also one of the main graphite supplies of the world.

Passau is a picturesque town, situated on a tongue of land formed by the confluence of the Danube and the Inn Rivers. It lies near the Austrian border and owes its importance to the Danube navigation. The Bavarian forest extends westward from Passau and finds a continuation in the more extensive Bohemian forest, and both cover large deposits of gneiss and granite. Although graphite is commonly present in the vicinity of these minerals and traces of it have actually been found in the area named, it is only in the neighborhood of Passau that the valuable deposits are situated. These have been utilized for several centuries and crucibles made of Passau graphite were used by the alchemists of the Middle Ages.

Two principal varieties of graphite are known to commerce—the hard and the flaky. The Passau deposits belong to the second class. Although the hard kind is more valuable, the supply thereof constitutes only 5 per cent of the total amount of graphite mined in the world. Ceylon furnishes most of the flaky variety: in 1912 it exported over 30,000 tons, worth about \$3,000,000, Germany taking one-fourth of the total shipments. The price is constantly rising, not by reason of speculation, but because the more available supply is being gradually exhausted. Aside from Ceylon, Madagascar has recently entered the graphite market, but its supply is inferior to that of Ceylon in quality and difficult to refine.

Rising prices will eventually induce capitalists to give more consideration to the Passau deposits. These were described at length in a recent number of the Bavarian official organ, *Bayerische Staatszeitung*, by Dr. E. Weinschenk, professor of mineralogy at the University of Munich. "The graphite deposits in the neighborhood of Passau," he writes, "represent without doubt an enormously rich territory which, if properly worked, will be a source of wealth and prosperity for centuries to come."

Figures given in the official Statistical Annual for Bavaria indicate an output in this kingdom in 1910 of 7,415 tons, value, \$74,613; in 1911, 11,298 tons, value, \$71,067; and in 1912, 12,532 tons, value, \$79,801.

The fact that the deposits underlie the properties of numerous small farmers, in whom the mineral rights vest, has retarded their development.

The Passau graphite is of superior quality, adapted

to the manufacture of the finest crucibles used in the smelting of copper, bronze, brass, and the precious metals. Crucibles for making steel castings need not be so good, and the graphite of which they are made is mined in Bohemia, Moravia, Lower Austria, and Styria, as well as in Italy and Finland. It is only one-tenth as costly as the Passau product. This circumstance has caused German black lead to be regarded as a cheap and inferior variety, thereby occasioning the supposition that the graphite mined at Passau must be of poor quality since it comes from Germany.

While not so fine as the Ceylon graphite, that of the Passau region can be refined without great expense (provided this be done by a mining company with sufficient capital), and the character of the deposits renders their exploitation fully as profitable as those of the island named. The Passau graphite is not mixed with granite, but is found interbanded in gneiss. Although it never contains more than 65 per cent of pure carbon, the fact that it can be quarried renders the cost of its mining so small compared with the Ceylon product that it would doubtless prove a serious competitor of the latter if a well-organized and properly financed company were to undertake its exploitation.

CEYLON.

According to market reports a slight improvement has taken place in the tone of the plumbago market recently, though the business transacted is said not to compare favorably with plumbago sales at this season in former years. The trade depression is credited to a poor demand in the United States and also to a certain feeling of uneasiness owing to the reports of a large estimated output of plumbago in Madagascar.

One can not vouch for the facts as expressed in the plumbago market at present, as there are fairly authentic rumors of an attempt on the part of certain local firms to "bear" the market. A peculiar feature is that, though the demand from the United States is made to appear unnaturally small, nevertheless certain local dealers are attempting to buy stocks in Madagascar for import into Ceylon. As this island uses practically no plumbago, Madagascar stocks can be imported only for re-exportation to the United States or to Germany when better prices prevail. In other words, it is thought that these dealers will buy under cover on the local market while the prices are low, confident that in a very short time the demand from the United States and Germany will become much stronger.

An indication of the correctness of this is suggested from the fact that one of the largest firms interested in plumbago mines and mining in the island is said to have recently placed orders in Europe for the latest plumbago mining machinery. New machinery is also to be used in the mines of the Kurunegala district.

On the other hand, owing to the greatly restricted demand from the United States at the end of last year and during the past few months, numerous pits

in different parts of the island have either stopped work or are about to stop work. This is especially the case with regard to a large number of pits in the Southern Province, many of which ceased work in December last.

In his report for 1912-13, Inspector of Mines T. G. Hunter thus summarizes conditions in the Ceylon graphite industry last year:

Prices during the first 10 months were excellent. The market in this commodity has been very uneven for years and liable to heavy fluctuations. The average price is calculated officially at \$5.14 per hundredweight [112 lbs.] for the year 1913. In January there was a heavy rainfall, and in the Kurunegala district especially it was responsible for a considerable decrease in the output of plumbago, as several of the big mines that had not previously had water troubles were flooded for the greater part of the year.

There were several reports received stating that mines were being worked in a way that was likely to result in some injury to those employed in the vicinity, but in nearly all the cases it was found on visiting the place that there was a dispute between adjoining mines about the plumbago that was being mined. This is generally due to the fact that the various owners of a piece of land have given the right to mine to different people, who have sunk mines close to each other without determining any boundaries. There is no regulation at present to fix the distance apart at which mines shall be sunk.

NUMBER OF MINES AND WORKMEN.

The following table compiled from the half-yearly reports sent in for January, 1913, July, 1913, and January, 1914, shows the number of mines worked and the number of men employed; it is an average of the three periods:

Province.	Number of mines.	Number of men.
Western	222	2,277
Central	14	195
Southern	893	2,761
Northwestern	37	1,528
Sabaragamuwa	169	2,792
Total	1,335	9,533

UNITED STATES.

According to figures recently made public by the United States Geological Survey, the production of graphite in the United States in the calendar year 1913 consisted of 2,243 short tons of amorphous graphite, value \$39,428, and 5,064,727 lbs. of crystalline (flake), value \$254,328, or a total of 4,775 short tons, worth \$293,756, as against 3,835 tons, value \$220,583 in 1912, and 3,618 tons, value \$288,465 in 1911. This was supplemented by supplies of foreign graphite, the American imports (general commerce) of which during the fiscal years 1911, 1912, and 1913 were as shown in Table I:

TABLE I.

Imported from.	1911.		1912.		1913.	
Europe:	Tons.	Value.	Tons.	Value.	Tons.	Value.
Austria-						
Hungary ..	320	\$6,544	200	\$3,996	525	\$10,332
Belgium	2	128	5	186	1	25
France	1	53			16	365
Germany	25	1,409	33	2,641	115	3,766
Italy	578	7,758	430	6,674	323	5,846
Norway					1	30
United Kdm.	97	9,543	6	743	182	23,605
North America:						
Canada	1,972	85,724	2,481	95,355	1,874	120,656
Mexico	3,005	238,399	1,988	115,818	3,520	174,474
Asia:						
China	20	928				
British						
East Indies.	13,112	1,307,980	12,787	1,192,521	16,137	1,591,756
Japan	1,015	20,159	661	10,452	2,528	41,322
Total	20,156	\$1,678,625	18,591	\$1,428,386	25,222	\$1,972,177

In the fiscal year 1914 (for which period detailed figures are not yet available) the imports into the United States amounted to 24,868 tons, value \$1,846,126.

WORLD'S GRAPHITE PRODUCTION.

Table II of the world's production of natural graphite for the years 1909-1911 was compiled by the United States Geological Survey from "Mines and Quarries: General Report with Statistics, part 4." with quantities expressed in short tons:

TABLE II.

	1909.		1910.		1911.	
Country.	Tons.	Value.	Tons.	Value.	Tons.	Value.
U. S.*	8,243	\$345,509	4,202	\$335,443	3,618	\$288,465
Canada	863	45,999	1,392	74,083	1,269	69,576
Mexico	1,878	25,301	2,571	36,207	3,050	36,353
Russia		1,913	(†)	(†)	(†)	(†)
Germany ..	7,467	64,724	8,174	76,404	12,454	72,754
Austria	44,875	320,289	36,520	281,220	46,855	332,489
Norway						
Sweden	29	779	1,526	1,884	72	2,097
France			606	5,353	408	3,601
Italy	12,768	71,148	13,790	74,808	13,912	74,701
Japan	136	5,290	162	5,202	126	8,911
China					22	1,728
Chosen						
(Korea)		75,012		56,719		\$65,727
India	3,508	60,972	4,761	99,661	4,533	45,867
Ceylon	36,056	3,237,751	\$35,310	\$2,577,600	\$30,183	\$2,159,529
Madagascar	220		601	21,218	1,373	48,534
So. Africa.	3		40	6,755	44	6,365

*Exclusive of artificial graphite. †Statistics not available.
‡Export figures.

The proportions of the world's supply of plumbago used for various purposes can only be approximated. A prominent industrial authority, however, places the world's consumption of graphite for making crucibles at 55 per cent of the total; for stove polish, 15 per cent; foundry facings, 10; lead pencils, 5; paint, 5; lubricants, 5; and all other uses, 5 per cent. If the value rather than the quantity be considered, about 75 per cent of the world's consumption should be credited to crucibles.

Slag is largely used as railway ballast in the district of Lorraine Germany. About 250 miles, or two-thirds of the total mileage, are ballasted more or less completely with that material. It is used chiefly on roads that have been constructed or reballasted in recent years and especially on the roads over which traffic is heavy. On smaller, less used lines where the traffic is light, gravel or whatever suitable material is at hand is used. Slag costs about 14½ cts. per cubic yard at the furnace. It is regarded as economical ballast within a radius of 15 to 30 miles, but cannot compete with rock at a greater distance than that on account of the cost of transportation, except, of course, in places where no suitable rock ballast is to be found. It is said that the slag is far superior to gravel as ballast and that it is equal to the best variety of rock.

Pine and fir piles that have been in service for 43 years on a railway trestle in Great Salt Lake have, on inspection, been found perfectly sound, due to thorough impregnation with salt.

PROGRESS IN THE MANUFACTURE OF STANDARD ALLOYS.*

By LUMEN.

The history of the Lumen Bearing Co. furnishes an unusual example of the success that may be attained through careful management and good direction of organization, even in brass founding—a business filled with uncontrollable features in purchases and most susceptible to blundering competition in sales. Starting some twelve years ago, taking over the affairs and small foundry of the defunct predecessor, the present company began the manufacture and sale of Lumen bronze, the zinc base alloy so well known today among electric-motor and machine tool builders.

The capacity at that time, mainly Lumen, was about \$100,000 annually. With the plant enlarged to the present capacity, the annual capacity today is about \$2,000,000, an increase of 2,000 per cent. (Copper in 1901 averaged about 17 cts., tin about 27 cts., comparing today with 15 ct. copper and 40 ct. tin.)

The Lumen bronze attracted a great deal of favorable attention and brought inquiries for the copper-tin bronzes and various grades of brass. Entering into all branches of the non-ferrous casting business, the organization grew rapidly and soon demanded a chemical laboratory, a testing machine, and the application of the most modern ideas of scientific management. An order system, worked out to the smallest detail; a comprehensive cost system; the daily control of metals; and all the details of melting, molding, coremaking, cleaning, inspecting and shipping were carefully studied. Unnecessary data and details were dropped, to the betterment of efficiency and of service, and a "balance" of organization arrived at that makes it most readily possible to undertake each new cast-problem effectively—the most vital feature of a successful jobbing brass foundry.

The sales department is strong and active, its men being trained to work out bearing problems with the customer, with the aid of a capable engineer at Buffalo. The Lumen Bearing Co.'s booklets, and monthly metal reports are instructive and aim to extend broadcast interesting data about the non-ferrous alloys. These books are written by members of the organization, many of whom are graduate engineers.

The following table indicates the capacity of the plant in area, molding and melting.

Department—	Size.	Area.
Molding floor	55x189	10,395 sq. ft.
A1 molding floor.....	29x 49	1,421 sq. ft.
Total molding floor.....		11,816 sq. ft.
Babbitt room	31x 81	2,751 sq. ft.
Inspection room	32x 32	1,024 sq. ft.
Shipping room	32x 50	1,600 sq. ft.
Patt. shop	30x 30	1,500 sq. ft.
Patt. storage	24x 91	2,184 sq. ft.
Melting room	35x 77	2,695 sq. ft.
Core room (oven included).....	41x 65	2,665 sq. ft.
Core room capacity—		
14 core makers		
5 machines		

*From The Metal Industry.

Core room oven shelf area.....		430 sq. ft.
Storeroom	39x 53	2,067 sq. ft.
Total		36,000 sq. ft.
Moulders (machines, benches, floor) ..		60 sq. ft.
Furnace capacity per day—		
Oil	23,000 lbs.	
Machine shop	28x130	3,640 sq. ft.
Cleaning room	34x 75	2,550 sq. ft.
Carpenter shop	35x 43	1,505 sq. ft.
Coke	18,000 lbs.	
Aluminum	3,000 lbs.	
Babbitt	25,000 lbs.	
		69,000 lbs.

This table does not indicate the capacity for bronze and brass trolley wheels, or for die castings.

In addition to Lumen bronze the company has made a specialty of manganese bronze and has recently issued a special booklet entitled "High Tensile Bronze," covering this well known metal. Continual attention to detail is absolutely necessary in the manufacture of this metal, if a high strength, high grade material is to result.

A new booklet is in press, to be known as "Bronze Alloys," which will enumerate the most important metals giving physical properties, hardness, etc.

The company operates a branch plant at Toronto, Ontario, where the same plan of operation prevails as at Buffalo. The Toronto plant is the Buffalo plant on a smaller scale, making non-ferrous castings, trolley wheels, die castings and babbitts.

The output of Colorado mines during 1913, according to Charles W. Henderson, of the United States Geological Survey, was \$18,146,916 in gold, 9,325,255 ounces of silver, 87,620,364 lbs. of lead, 7,298,269 lbs. of copper, and 119,346,429 lbs. of zinc (in terms of spelter and zinc in zinc oxide), with a total gross value of recovered metals of \$35,449,298, as compared with \$37,320,966 in 1912, a decrease in value for 1913 of \$1,871,668, or 5 per cent. There was a decrease of \$441,646 in gold, an increase of 1,113,185 ounces of silver, an increase of 12,378,007 lbs. of lead, an increase of 190,966 lbs. of copper, and a decrease of 12,786,383 lbs. of zinc. The heaviest decrease in value was \$2,439,974 for zinc, but there were increases of \$582,031 for silver and \$469,394 for lead.

About 80 per cent of the output of fluorspar in this country is consumed as a flux in basic open-hearth steel furnaces. It is used also as a flux in blast furnaces, iron foundries, and silver, copper, and lead smelters; in the manufacture of fluorides of iron and manganese for steel fluxing; in the manufacture of glass, enameled, and sanitary ware and of hydrofluoric acid; in the production of aluminum; and for many other purposes.

Trinidad asphalt mastic is stated to have been found to be a satisfactory material for lining concrete tanks subject to action of sulphuric acid.

INTERNATIONAL SPECIFICATIONS ON PIG-IRON, AND CAST IRON TEST BARS.*

Reports from Great Britain bring details of the newly submitted proposals to the Council of the International Association for Testing Materials for standard specifications for pig iron, for cast iron pipe and for an international test bar for judging the quality of the metal entering into iron castings. These proposals are confined to the world's export trade.

THE CAST IRON COMMITTEE.

Last year preparations were made by the American members of the Committee on Cast Iron to visit Europe and to push the matter as energetically as possible. A committee meeting in Brussels on December 5, 1913, brought about definite proposals for pig iron, cast pipe and an international test bar. The proposals were originally drawn up on American lines, modified by the German members to suit the Continent, with co-operation from Belgium and France, and support was given by some British producers. With the exception of the test bar, however, the English members would not adopt the work thus prepared, but submitted a minority report to the council of the International Association.

A sub-committee on the preparation of standard methods of sampling and analysis for cast iron was authorized. The members for England are Messrs. J. E. Stead and F. W. Harbord; for Germany, the Krupp Laboratories; and for the United States, Dr. Hillebrand of the U. S. Bureau of Standards.

AN INTERNATIONAL TEST BAR.

Appended is the resolution on the subject of an international standard cast iron test bar adopted at the meeting of Committee 1 (b) at Brussels, December 5, 1913:

1.—In order to obtain a reasonable uniform test bar (arbitration bar) for judging the qualities of iron poured into castings with reference to existing systems of measurement, a bar shall be selected for testing transversely on supports 18 inches apart (45 cm.) and that the diameter of this round bar shall be 1.2 in. (30 mm.), the relation of length to diameter being 15 to 1 as nearly as may be.

2.—The bars shall be cast in dry-stand moulds, vertically and with top pour. They shall be cast 20 in. (50 m.) long, and be rounded at the bottom. The load in testing shall not be applied faster than three seconds for every hundredth part of the diameter. For every specification mixture two moulds with three test bars each shall be cast, the bars to be cold before removal from the moulds which should have attained the shop temperature before pouring. The bars shall be brushed clean and not rumbled.

EXPORT SPECIFICATIONS FOR PIG IRON.

At the meeting of Committee 1 (b) at Brussels, as referred to above, the following was adopted for rec-

ommendation to the Council of the International Association:

1.—It is proposed that for international trading purposes in pig iron, the analysis be taken as the basis, inasmuch as the value depends upon its content.

2.—The following specifications for pig iron are recommended where the customary trade designations are insufficient (see accompanying tables). For silicon a variation of 0.25 per cent from analysis asked for, either way, shall be allowable. For sulphur and phosphorous the maxima given shall govern. For manganese a variation of 0.20 per cent either way shall be allowable.

It was resolved that the code words above given are to be specially recommended as most useful for international commerce in pig iron.

The English members of Committee 1 (b), while concurring in the specifications for cast iron test bars, did not accept the above pig iron specifications but instead suggested the following:

Grade 1—		Per cent.	
Silicon		2.5 to 3.5	
Sulphur, max.		0.05	
Silicon.		Sulphur.	
Per cent.	Code.	Per cent.	Code.
0.50.....	La	0.02.....	Sa
0.75.....	LaX	0.03.....	Se
1.00.....	Le	0.04.....	Si
1.25.....	LeX	0.05.....	So
1.50.....	Li	0.06.....	Su
1.75.....	LiX	0.07.....	Sy
2.00.....	Lo	0.08.....	Sh
2.25.....	LoX	(Maximum)	
2.50.....	Lu		
2.75.....	LuX		
3.00.....	Ly		
3.25.....	LyX		
3.50.....	Lh		
3.75.....	LhX		

Variations 0.25 either way allowable.

Phosphorus.		Manganese.	
Per cent.	Code.	Per cent.	Code.
0.050.....	P	0.20.....	Ma
0.100.....	Pa	0.40.....	Me
0.250.....	Pe	0.60.....	Mi
0.500.....	Pi	0.80.....	Mo
0.750.....	Po	1.00.....	Mu
1.000.....	Pu	1.25.....	My
1.500.....	Py	1.50.....	Mh
2.000.....	Ph		

(Maximum)

Variation 0.20 either way allowable.

Phosphorus, max.		1.750
Manganese		0.40 to 1.00
Grade 2—		
Silicon		2.0 to 3.0
Sulphur, max.		0.08
Phosphorus, max.		1.750
Manganese		0.40 to 1.00
Grade 3—		
Silicon		1.5 to 2.5
Sulphur, max.		0.12
Phosphorus, max.		1.750
Manganese		0.40 to 1.00

Committee 1 (b) also recommended international specifications for cast iron pipes and fittings. From this the English members also dissented.

The production of crude barytes in the United States in 1913 was 45,298 short tons of 2,000 lbs., valued at \$156,275.

*From the Industrial World.



METHODS OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR INSTITUTE OF TECHNOLOGY.

Analysis of Alloy Machinery Steels. (Concluded.)

COPPER.

Copper is determined by essentially the method described in circular of the Bureau of Standards No. 14. A 10-gram sample of the steel is treated with about 200 c.c. of 10 per cent sulphuric acid at about 80° C. until all the iron has dissolved. All of the copper remains undissolved by this treatment. The solution is then filtered off and the residue carrying the copper is washed free from iron by means of a warm 2 to 3 per cent solution of sulphuric acid saturated with hydrogen sulphide. The function of the hydrogen sulphide is to prevent the oxidation of the copper to CuO and consequent solution in the sulphuric acid.

The following two methods give good results:

(1) The precipitate is washed through the paper with boiling hot dilute nitric acid (1:1), followed by hot water, the minimum volume to assure complete solution of the copper being used. A few cubic centimeters of bromine water is then added and the whole boiled thoroughly. This accomplishes the removal of the oxides of nitrogen, any possible hydrogen sulphide, and finally the excess of bromine. Ammonia is added to alkalinity, the excess removed by boiling, and the whole made acid with dilute acetic acid. After cooling, 20 cubic centimeters of a 15 per cent solution of potassium iodide is added, the whole allowed to stand five minutes and the liberated iodine titrated with a solution of sodium thiosulphate of about twentieth normal strength. The thiosulphate solution should be standardized directly against pure copper, the treatment of the sample, following its solution in nitric acid, being the same as that in the determination.

(2) The filter paper with the precipitate of copper is incinerated in a porcelain crucible, preferably in a muffle, the residue digested in nitric acid, transferred to a platinum crucible, sulphuric and hydrofluoric acids added to expel silica, and the whole evaporated to fumes of sulphuric acid. The solution is then diluted and the copper precipitated electrolytically in the usual manner.

MOLYBDENUM.

Molybdenum is determined according to the method described in circular of the Bureau of Standards No. 14. The 5 to 10 gram sample is dissolved as in the treatment for copper as outlined above and after fil-

tering off the copper the solution is saturated with hydrogen sulphide, the residue filtered off on an asbestos felt in a Gooch funnel and washed with the very dilute sulphuric acid containing dissolved hydrogen sulphide. The residue contains molybdenum sulphide. It is digested with aqua regia, the solution filtered after dilution, and to the filtrate sulphuric acid added and the whole evaporated to the complete expulsion of other acids. The residue is taken up with water and a little sulphuric acid (if the latter is necessary for complete solution), and the solution saturated with hydrogen sulphide in the cold. Complete precipitation is best attained by placing the solution thus saturated in the cold, in a pressure bottle and heating it for some time in boiling water.

(1) The precipitate is molybdenum sulphide. It is filtered upon a Gooch crucible, ignited in a muffle at a low red heat, and the resulting MoO₃ weighed. Weight of MoO₃ multiplied by 0.6667 gives molybdenum.

COBALT.

This metal is occasionally found in alloy steels. Its determination depends upon the electrolytic deposition of nickel and cobalt together and the subsequent determination of nickel by the dimethyl-glyoxime method as described in a previous article.* From the weight of the nickel and cobalt together, the weight of cobalt is obtained by difference. The procedure follows: The 2-gram sample is dissolved in minimum quantity of aqua regia and the nitric and hydrochloric acids replaced by sulphuric acid and evaporation to copious fumes of sulphuric anhydride. The residue is taken up with water, care being exercised that all salts be dissolved. Ammonium hydroxide is then added in considerable excess, and the solution electrolyzed without removing the precipitate. A gauze electrode is best. The conditions of electrolysis are: A current of about 1 ampere for an hour, when the current is raised slowly up to about 3 amperes and held there for about two hours. The potential is about three to three and one-half volts. Three hours' electrolysis should give complete precipitation. It is well to test for its completeness by taking a small portion of the solution, making it nearly neutral with hydrochloric acid and adding a drop or two of dimethyl glyoxime. A red precipitate indicates the presence of nickel, and consequent lack of complete removal of that metal. If the nickel is all deposited, the cobalt may be assumed to be. The electrode, after complete precipitation of the metals, is removed from the so-

*This Journal, Vol. xx, No. 1, p. 10, July, 1914.

lution, washed first with water and then with alcohol and dried at a temperature of not more than 100° C., and the weight of nickel and cobalt taken. The deposited metals are dissolved from the cathode by digesting the latter for not less than fifteen minutes with hot, 1:1 nitric acid. The solution of nickel and cobalt nitrates is then analyzed for nickel as previously described. By the above method of electrolytic determination, a little iron is included in the precipitate of metals. The weight of this may be corrected for by evaporating the filtrate from the dimethylglyoxime precipitate with sulphuric acid to destroy the excess of the precipitant, taking up in water and determining iron either gravimetrically by double precipitation with ammonia, or colorimetrically with potassium thiocyanate.

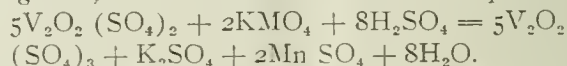
VANADIUM.

The method employed is essentially that described in circular of the Bureau of Standards No. 14.

The 10-gram sample is dissolved in hydrochloric acid (1:1), a few drops of hydrofluoric acid added, and the whole thoroughly boiled and filtered.

The residue, which will carry some vanadium, is ignited in platinum, and fused with sodium carbonate, the fusion extracted with hot water, the insoluble portion filtered off, and filtrate containing some sodium vanadate added to the main chloride solution. This solution is then oxidized by boiling with a little nitric acid, and the free chlorine and oxides of nitrogen boiled off. The chloride solution is cooled, transferred to a separatory funnel, an equal volume of ether added, and the whole shaken cautiously, care being taken to keep the mixture cool by occasionally immersing the funnel in cold water. Finally, it is allowed to stand until two distinct layers form and the aqueous layer tapped off. About 30 c.c. of 1:1 hydrochloric acid is added to the ether solution, and the whole shaken, allowed to stand, and the aqueous layer added to the previous aqueous solution. This process separates all but one or two per cent of the iron from the other metals, through the solubility of ferric chloride in ether. The aqueous solution is evaporated on the water bath to expel the small quantity of ether in it, concentrated nitric acid added, and the whole evaporated to dryness. The dry residue is taken up in concentrate nitric acid (avoiding large excess), diluted with water, and nearly, though not quite, neutralized by the addition of strong sodium hydroxide solution. It is then poured slowly, with constant stirring, into about 200 c.c. of a 10 per cent sodium hydroxide solution. The precipitate of metallic hydroxide holds some of the vanadium, so it should be redissolved in nitric acid and reprecipitated as before by means of sodium hydroxide, smaller volumes of the hydroxide solution being used. The combined filtrates contain the vanadium as sodium vanadate. It is nearly neutralized by nitric acid (dilute) and an excess of mercurous nitrate solution added. This precipitates mercurous vanadate quantitatively. The precipitate is

filtered, washed with dilute mercurous nitrate solution and dried. The paper is burned (preferably separately from the precipitate) and the precipitate ignited in a platinum crucible until free from mercury. This gives impure V_2O_5 . This vanadium pentoxide is fused with a little sodium carbonate, fusion extracted with water and the insoluble matter filtered off through an asbestos felt (Good crucible). From the sodium vanadate solution, mercurous vanadate is precipitated and converted into V_2O_5 as before. The purified pentoxide is then fused with sodium carbonate again. The fusion is taken up in dilute sulphuric acid, and the vanadic sulphate reduced to di-vanadyl sulphate ($V_2O_2(SO_4)_2$ corresponding to V_2O_4) by sulphur dioxide. The excess of reducing agent is completely removed by heating and passing carbon dioxide through the solution in a flask. Finally the di-vanadyl sulphate is titrated at about 60 C. with fiftieth normal permanganate, to the vanadic condition. The equation is:



Since $2KMnO_4 = 10 \text{ Fe}$ and $2KMnO_4 = 10$

51.2

55.9

51.2

then 1 V = 1 Fe and the vanadium standard is —

55.9

or 0.9142 times the iron standard.

TITANIUM.

Five grams of the sample is dissolved in 40 c.c. of hydrochloric acid (sp. gr. 1.05). The insoluble matter is filtered off, washed with water, ignited in a platinum crucible, and treated with hydrofluoric and sulphuric acids to eliminate silica. The residue is fused with sodium carbonate, the fusion dissolved in water, the solution filtered, and the insoluble material dissolved in sulphuric acid. A sufficient amount of ferric alum is added to a standard titanium solution to give the same tint as the sample when they are at the same dilution (for the residue from the silica always contains a little iron along with the titanium). Hydrogen peroxide is added to the solution of the sample prepared as described and to the standard titanium solution, with the added ferric alum, the color of these solutions is then compared in a colorimeter. From this comparison, and the known value of the standard titanium solution, the titanium content of the sample under examination is calculated.

Sugar Output of Cuba in 1914.

The sugar crop of Cuba for the season of 1914 will, by allowing conservative further production to mills still grinding, reach at least the total of 2,575,000 tons. If the weather remains of a normal character for the remainder of the rainy season, the U. S. Consul General at Habana predicts the production will in all probability go still higher, and may surpass 2,600,000 tons, which will represent a gain of about 175,000 tons over the great crop of the year preceding.

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NOTES AND COMMENTS.

Autumn Meeting of the American Chemical Society Canceled.

The autumn meeting of the American Chemical Society, which was scheduled to occur at Montreal, Sept. 15 to 18 inclusive, has been cancelled.

This action has been taken on account of the European troubles and the resultant difficulties which would attend the meeting of any number of people from any other country in a colony of one of the countries involved in war.

This is the first semi-annual meeting of the American Chemical Society which has not occurred according to schedule.

It is probable that many other similar gatherings will be interfered with before hostilities are over.

It is unlikely that peace and stable conditions will come in time for the 9th International Congress of Applied Chemistry to be held in St. Petersburg during August, 1915.

American Chemical Industries and the European War.

It is too early as yet to say with any degree of assurance just what will be the lasting effect of the present European conflict on the chemical industries of America.

It is not difficult, however, to foresee some of the more immediate effects.

Practically all our laboratory wares such as glass-ware, porcelain ware, and organic reagents are im-

ported from Germany. Of course, all such importations are now at an end. There is never a very large stock of such materials in the hands of American jobbers, so the supply is strictly limited and many of the jobbers have already canceled all quoted prices.

Many of the schools and colleges import, during the summer, the laboratory supplies needed for the ensuing year; those whose importations are now in this country can consider themselves fortunate for it is probable that many laboratories will lack necessary equipment during the coming year.

Certain chemicals come to us almost exclusively from European sources. Among these may be mentioned the compounds of potassium, extensively used in fertilizers; magnesite, used as a refractory material in the steel industry and in compounding certain plastic masses.

This country has been explored, almost microscopically to discover a source of soluble potassium compounds and none has been found. We can therefore believe that there will be no development of the manufacture of such compounds in this country *unless* the European markets shall remain closed for some time. It is possible then that some of the proposed processes to obtain soluble potassium compounds from feldspar will be brought to commercial success. There will be no great shortage in the fertilizer market for some months, however, as most of these goods are made and sold during a certain period of the year and this is some months away.

There are deposits of magnesite in this country which will be developed as soon as the price for the imported material rises to a point where domestic production will be profitable, so no shortage of this material will occur, although there will undoubtedly be a sharp rise in price.

Some of our alloy steels have been imported but an increased domestic production can take care of this.

It is in the line of certain of the benzene derivatives where the most possibilities exist for profitable American manufacture, with the German ports closed. We also have the necessary raw materials for such lines of manufacture and also probably have the necessary technical knowledge.

To build up a stable and profitable manufacture of these compounds would necessitate that the European, particularly the German, supply must be withdrawn from the market for a number of years. The likelihood of this occurring is *very* problematical, so it is not likely that our American manufacturers will hasten into these industries.

Some of our chemical industries have already been adversely affected by the war.

Petroleum exports have fallen off very materially and it is reported that one great refinery for the export trade is to close.

Our exports of certain wood distillation products are also sure to be curtailed.

In certain lines such as the jobbing and refining of tropical and semi-tropical oils and fats, carried on very extensively in Germany and France, there is sure to be a readjustment of trade conditions and there is every reason to believe that we can secure and hold a very large part of this business.

It may be said in general that any continuation of the present European conflict can only have a marked stimulating effect on American chemical manufacture.

We are in a position, both as regards raw materials and technical knowledge to enter very largely into the various lines of chemical manufacture and to secure satisfactory profits.

Growth in Chilean Nitrate Industry.

The U. S. Consul at Valparaiso reports that the nitrate business of Chile is in a prosperous condition and has a bright future, since new machinery, processes, and methods make it possible to work profitably much lower grade deposits than formerly. Even the tailings in many cases are worked at a good profit. New works are being opened and the returns for the nitrate year ending June 30, 1914, promise to be even better than in 1913, when production increased about 5,000,000 Chilean quintals (Chilean quintal = 101.41 lbs.). The consumption of nitrate is increasing very rapidly, having been 55,522,168 quintals during the first 10 months of the nitrate year 1914, beginning with the first of last July, against 50,545,964 quintals for a like period during 1912-13. In this the United States is more than holding its own. The southern part of the nitrate fields, of which Antofagasta and Mejillones are the centers, is developing more rapidly than any other part. The exports from these ports for the first four months of 1914 exceeded the exports of the same period of 1913 by 25 per cent. The development in this industry has created a demand for up-to-date machinery and methods which it will pay American manufacturers to study. Some new American machinery is being installed, but since much of the capital invested in this industry is English, machinery from that country has the preference, unless active propaganda work is done by American manufacturers.

International Petroleum Commission.

It is possible that the third General Congress of the International Petroleum Commission announced for Bucharest, Roumania, Sept. 26 to Oct. 2, 1914 may be postponed. The work of the congress was to be divided into the following sections: Methods of analysis, nomenclature, and storage transport. The general object of the commission is to study the unification of the methods of analysis and the nomenclature of petroleum and its derivatives, and the conditions of storage and transport, bearing in mind the interests of trade, industry, customs and public security, and to secure international agreement on these matters.

THE NITRATE INDUSTRY IN 1913.

According to the American Fertilizer there were extensive improvements made in the nitrate industry of Chile during 1913, both in methods of handling the raw materials and in the number of up-to-date nitrate plants, which called for large quantities of new machinery, and the outlook for 1914 indicates that much is to be done to reduce the cost of production, in which the Government is to take a hand. In November it was decided to move the headquarters of the nitrate propaganda from Iquique to Valparaiso, and the general tendency of the nitrate business is southward. In 1905 24,280,545 quintals (1 quintal = 101.41 lbs.) of the total of 35,910,332 quintals exported from the country were shipped from Parapaca, of which Iquique is the center. During last year the shipments from Valparaiso were 22,844,650 quintals out of a total of 59,528,207 quintals. The headquarters of practically all of the nitrate producers and the nitrate dealers are in Valparaiso, and the nitrate ports of the North are really only way stations for loading the nitrate as per orders sent from Valparaiso.

The nitrate interests in Chile enjoyed a prosperous season, with exports amounting to 59,528,207 Chilean quintals, against 54,168,875 quintals for 1912, with a good outlook for 1914. The price of nitrate varied from \$1.95 per quintal for the first week in January to \$1.98 at the close of December, 1913.

The United States took more nitrate during 1913 than in any like period, having reached 13,464,128 quintals, against 10,444,411 quintals for 1912. The United Kingdom took 21,433,997 quintals; Germany, 13,633,556 quintals; France, 2,594,575 quintals; Belgium, 2,633,277 quintals; Netherlands, 2,173,610 quintals; Japan, 616,110 quintals; and Italy, 232,236 quintals.

The exportation of nitrate for the first eight months of the nitrate year, from July 1, 1913, to March 1, 1914, was 42,027,526 Chilean quintals (Chilean quintal equals 101.42 lbs.), against 42,263,589 quintals for the same time for 1912-1913 and 40,142,072 quintals for a like period during 1911-12. The price of nitrate continues fair at \$1.83 per quintal.

WANTS.

POSITION WANTED:—By young man, with good theoretical training, and 4 years' first class laboratory experience in general inorganic analyses; position as chemist or assistant; moderate salary. Apply Box L. Chemical Engineer, 608 So. Dearborn St., Chicago, Ill.

POSITION OPEN:—Assistant Chemical Superintendent; must have had actual previous practical experience in the manufacturing end of a company making heavy chemicals; must be an American; a graduate of chemistry or chemical engineering; age 30 to 40 years; salary \$1,800-2,400. The Engineering Agency, 1662 Monadnock Block, Chicago.

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No. 3.

POTASH SALTS: SUMMARY FOR 1913.*

Compiled by W. C. PHALEN, United States Geological Survey, Washington, D. C.

The activities of the United States Geological Survey in the investigation of potash salts during 1913 were more restricted than in previous years. In the field, drilling was carried on in two areas, Columbus Marsh and Black Rock Desert, Nevada, but it was of short duration, owing to the inaccessibility of the area for an unusually long period of the year, on account of the heavy rains, which made it impossible to transport apparatus to the drill sites. A general plan involving the stratigraphic study of the so-called "red bed" salines of certain of the Southwestern States, including New Mexico, Arizona and Utah, was begun by N. H. Darton, and several months of field work was done. A brief review of certain basins in the Great Basin region of California and Nevada was made by H. S. Gale in the further general study of the hypothesis that potash deposits may be found in desiccated lake basins.

In the laboratory, attention has been directed to a few definite problems indicated by the preceding general experimental work.

POTASH SALTS IN THE GREAT BASIN REGION.

Deep Drilling Explorations.

In addition to the drilling explorations carried out by the Survey and mentioned in the introductory paragraph, the Railroad Valley Co., of Tonopah, Nev., did some deep drilling during the year. Since this company began operations, more than two years ago, it has drilled more than 10,000 ft. in seven wells located in Railroad Valley, Nye County, Nevada.

During July, 1913, the company in its well No. 2 encountered buried soda-bearing beds made up chiefly of the mineral gaylussite ($\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot 5\text{H}_2\text{O}$). These were penetrated a distance of 127 ft. without reaching bottom. Since potash salts are more soluble than the mineral gaylussite, they would in a normally deposited saline series overlie that mineral. On this basis it was assumed that they did overlie the gaylussite in some other part of the basin, namely, in the

deepest part, in which, consequently, they would cover a smaller area than the gaylussite deposits. In the work the gaylussite bed was counted on as furnishing a datum plane to aid in tracing the contours of the basin, and hence in locating the deepest part in which the potash salts were expected to be found. Proceeding on this hypothesis, four additional wells were drilled, but without conclusive results. Two of these wells did not encounter the gaylussite deposit at all. It was also found that the upper portion of the gaylussite beds was flatter and more variable than was expected—conditions which rendered precise correlation and determination of contours impossible. Operations on the seventh well drilled had to be suspended before it reached the depth at which the hoped-for data were expected to be obtained.

The gaylussite beds were encountered only in wells Nos. 2, 4 and 6. In No. 2 they were penetrated a distance of 127 ft. in well No. 6 a distance of 194 ft. and in well No. 4 a distance of only a few feet. In no well was the gaylussite drilled through, but it was found to be purer and more solid toward the bottom. The precise correlation of the two gaylussite deposits found—the one in well No. 2 and the other in well No. 6—was not considered possible, and it was also found impossible to establish synchronism between any two particular beds of wells No. 2 and No. 6. Still, there seems little doubt that the gaylussite series of wells No. 2 and No. 6 are synchronous and represent the same stage of concentration of the same saline solutions.

The most important question confronting the company at present is whether well No. 6 is in or near the deepest depression, or whether such depression lies an unknown distance to the south. This doubt can be settled only by further drilling. If such drilling indicated no southward extension of the basin, the chances of finding important segregations of potash salts are very slight. If it be proved that the basin does extend farther to the south, then probably several wells will have to be drilled to obtain some idea of its size and character and of the existence of other saline deposits in it.

In the event that no potash salts are found, it is possible that the gaylussite bed itself may be of value. The extent of this bed will have to be ascertained by

*From the American Fertilizer.

drilling, and methods will have to be devised both for mining it and for producing soda from it.

The report of E. E. Free, consulting geologist to the Railroad Valley Co., from which these data were obtained, was transmitted January 2, 1914. This report contains, in addition to the information given, a map showing the location and records of the wells, together with an appendix describing gaylussite and its possible utilization.

It is reported that the Nevada Potash Co., with headquarters at Goldfield, Nev., plans to explore Clayton Lake, 20 miles west of Goldfield.

EXPLANATION OF THE TERM "POTASH."

To meet the numerous inquiries that have been addressed to the United States Geological Survey regarding the exact meaning of the terms "potash," "actual potash" and "potassium," the following explanation is given:

The element potassium, represented by the symbol K, is the basis of all potash salts or compounds. This substance is a metal; that is, it possesses metallic properties. To prevent rapid change it must be kept from air and water, with both of which it combines with great avidity. Combined with oxygen it forms potassium oxide, represented by the symbol K_2O , known as potassa, but popularly as "potash." In estimating the quantity of potassium in the different products of the Stassfurt deposits, this compound, K_2O is employed as a standard, the object being to establish a basis of comparison for all potassium salts. Among chemists as well as laymen there has grown up the practice of using for this standard the term "potash." When only the term "potash" is used in speaking of potash products, it is understood to refer to the potassium oxide (K_2O) present. As a matter of fact, however, potash salts are not sold in the form K_2O , but as the sulphate or the chloride.¹ By the term "potassium sulphate" is meant potassium (K) combined with the acid radicle of sulphuric acid (SO_4), or potassium oxide (K_2O) combined with sulphur trioxide (SO_3), making the compound K_2SO_4 . By "potassium chloride" is meant potassium (K) combined with another element, chlorine (Cl).

In Table I are given the percentages of the element potassium and also the combination known as potash in or obtainable from the common potassium compounds and minerals:

DEVELOPMENT OF SALINE POTASH DEPOSITS.

California—Searles Lake.

A description of the saline deposits of Searles Lake, Cal., was published in this report for 1911.²

Searles Lake, known also as Borax Flat, is a dry lake basin much like many other desert basins in the Western arid region. It is a broad, somewhat circular valley or depression lying between the Slate and Argus ranges in the extreme northwestern part of San Ber-

nardino County and near Kern and Inyo Counties. The camp known as The Borax is about 25 miles by road from Searles postoffice, formerly Garden station, near the Mohave-Owenyo branch of the Southern Pacific Railroad. Searles Lake at present may be reached by the regular stage that runs from Johannesburg by the way of Garden station, or Searles, to Searles Lake, and thence on to Ballarat and Skidoo.

Searles Lake for many years was an important source of borax. Later the California Trona Co. was organized to produce soda ash from the deposits, and the lake has now become of interest in connection with the contemplated exploitation of its potash-salts deposits.

The announcement of Searles Lake as a possible

TABLE I—POTASSIUM AND "POTASH" IN POTASSIUM COMPOUNDS.

Name.	Symbol.	Percentage of Potassium (K)	Chemical Equiv. K_2O
Element:			
Potassium	K	100	120
Potassium salts or "potash salts":			
Pot. chloride (mineral sylvite)	KCl	52	63
Pot. muriate (same as chloride).			
Pot. sulphate	K_2SO_4	45	54
Pot. nitrate (saltpeter)	KNO_3	39	47
Pot. carbonate*	K_2CO_3	57	68
Pot. hydrate or caustic potash	KOH	70	84
Pot. cyanide	KCN	60	72
Stassfurt minerals:			
Carnallite	$KMgCl_3 \cdot 6H_2O$	14	17
Kainit	$MgSO_4 \cdot KCl \cdot H_2O$	16	19
Sylvite (potassium chloride)	KCl	52	63

*The term "potash" is often applied to this compound.

source of potash salts was made as the result of the collection and analysis of a set of brine samples from it in March, 1912, by E. E. Free, then of the United States Bureau of Soils, and Hoyt S. Gale, of the United States Geological Survey. A notice was at that time given to the press stating that reports which had been received concerning the unusually high potash content of the brine in this deposit were apparently confirmed by the results of these tests. Analyses of six brine samples taken at considerable depth in old wells at points distributed over the main salt flats showed that an average of 6.78 per cent of the total dissolved salts was potash (K_2O), corresponding to 10.73 per cent potassium chloride (KCl). The individual results obtained were 7.63, 6.23, 6.89, 6.06, 7.27 and 6.57 per cent. The uniformity of these results seemed to indicate, although it did not prove, homogeneity in composition of the brine throughout the salt deposit. Based in part on the logs of the wells that had already been drilled, a statement was also made at that time that "existing data give reasonable assurance that the brine-saturated salt body is at least 60 feet thick and covers an area of at least 11 square miles. On the assumption that the salt constitutes 25 per cent by volume of the brine, the total amount of potassium oxide available is estimated as over 4,000,000 short

¹The chloride is also known in the trade by the chemically obsolete term "muriate of potash."

²Gale, H. S., Potash salts: U. S. Geol. Survey Mineral Resources, 1912, pt. 2, pp. 884-889, 1913.

tons (equivalent to approximately 6,000,000 tons of potassium chloride). This estimate is based on incomplete data, but it is believed to be conservative."

During the year 1913 the American Trona Co. was incorporated to operate works for refining and marketing the different saline constituents of the Searles Lake deposits. It is proposed to spend \$3,000,000 in completing a railway from Searles to the lake and in building a plant to have a capacity of 2,000,000 gallons of brine a day.

Many deep drillings have been made at Searles Lake by the company, and the study of many hundred samples secured has enabled those in charge of the enterprise to devise a process for the treatment of the salines.

The new works will draw from the lake approximately one-tenth of an inch of brine a day; the natural evaporation is much larger, and varies from one-fourth to one-half of an inch a day. The plan of treatment consists in first precipitating the soda as the bicarbonate. The next step involves crystallization in furnaces of simple type but large capacity. The process has been worked out with considerable care, but to insure against possible loss an initial unit with a capacity equal to 1 per cent that of the final plant will be erected and placed in operation before the main plant is built. It is expected that the daily output of the plant will be: Borax, 225 tons; soda ash, 508 tons; salt, 1,507 tons; sodium sulphate, 593 tons, and potassium chloride, 489 tons. The company will depend for its revenue mainly on the potash salts, the soda ash and the borax. The salt may ultimately be marketed, and it is possible that at some future time a use will be found for the sodium sulphate; but for the present these constituents are not taken into account.³

According to the latest information, the experimental unit referred to above is nearing completion, and it is expected to be ready for operation in the latter part of 1914. The 31-mile railroad from Searles on the Nevada & California Railroad (Southern Pacific) is completed to the new town of Trona, where the new works are being built. It is expected that 20,000 gallons of brine will be handled daily at the new plant, and that the works will be enlarged at a later date. It is unlikely that the salts from the Searles Lake deposit will enter the market regularly until the latter part of 1914.⁴

Oklahoma.⁵

Common salt is found in what are generally termed "salt plains" in Oklahoma, that is, over broad areas in which incrustations of salt occur. This common salt has come from springs, which flow at particular places, or from saline ground waters, which permeate the soil below the saline crusts. Such saline ground waters may also have originated in springs with subterranean outlets. Most of the salt is supposed to have come from salt beds in the so-called "red beds."

One group of these salt plains is found in Jackson County. This group numbers three in all, lying close together on the west side of Sandy Creek, about three miles from its mouth and approximately the same distance south of Eldorado. The northern plain lies in the E. $\frac{1}{2}$ sec. 31, T. 2 S., R. 23 W., the middle one in the NE. $\frac{1}{4}$ sec. 5, T. 3 S., R. 23 W., and the southern plain in the NW. $\frac{1}{4}$ sec. 5 of the same township and range. All three plains are on small tributaries which flow northeast into Sandy Creek. The northern and southern plains are each about 100 yards wide and 400 yards long; the middle plain is only 40 yards wide, but is one-fourth of a mile long. The sandy floor of the plains is covered by a thin saline incrustation, and the water does not seem to be saturated.

The analyses of the soluble salts which have been made by the Oklahoma Geological Survey are not given in detail in the reference cited. According to Snider, the analyses that have been made indicate the presence of much more sodium sulphate than sodium chloride; the potassium sulphate is also high. In the incrustation from the middle plain the proportion of sodium chloride is greater than in the two others, and there seem to be sufficient sodium and potassium sulphates to make the commercial recovery of common salt a question. It is possible that the potassium sulphate from the middle plain may be utilized as a by-product.

Texas.⁶

In the search for a deep source of potable water at Spur, Dickens County, Texas, a deep well has been drilled by S. M. Swenson & Sons, of New York. The total depth of the well is reported as nearly 4,500 ft. The upper 900 ft. of strata penetrated consist chiefly of red sand beds of shale, gypsum and anhydrite and two beds of rock salt, each about 10 feet thick and both more than 500 feet from the surface. Below the 900-foot level occurs a 250-ft. bed, consisting chiefly of fine sand, silt and salt, the proportion of salt varying from 20 to 60 per cent. From the 1,250-ft. level to the 2,050-ft. level the character of the rock passed through is not known from samples, but is thought to consist chiefly of dolomitic limestone. Below this is found red silt or clay, dolomitic and shaly limestone, and anhydrite; then dolomitic limestone; then very pure anhydrite. At 3,060 ft. a dark gray soft shale was met.

The presence of so much anhydrite and salt in the section led to the suggestion by J. A. Udden, of the Bureau of Economic Geology and Technology of the University of Texas, of the possibility of the presence of potash salts in the deposits. The well had in the meantime been cased below 1,300 ft. A sample, however, was taken after the water had been bailed to a depth of 2,200 ft. This sample was examined by S. H. Worrell, also of the bureau, with the following results:

³Min. and Sci. Press, June 14, 1913, p. 888.

⁴Eng. and Min. Jour., vol. 97, No. 9, p. 484, Feb. 28, 1914.

⁵Snider, L. C., Oklahoma Geol. Survey Bull. 11, pp. 213, 214, 1913.

⁶Udden, J. S., Potash in the Permian rocks of Texas: *Am. Fertilizer*, Dec. 14, 1912, pp. 40-41.

ANALYSIS OF WATER FROM WELL AT SPUR, TEXAS.

	Grains Per Gal.
CaSO ₄	1,688.4
CaCl ₂	814.1
MgCl ₂	263.2
NaCl	4,095.0
KCl	389.2
	7,249.9

The potassium chloride, therefore, amounts to 6.65 grams per liter, and constitutes more than 5.4 per cent of the total salts. As this amount of potash salts is somewhat high for a natural water, arrangements were later made for obtaining samples from different depths below the foot of the casing (1,350 feet). Fourteen samples were next obtained and tested for potash salts, but in only one of them, namely, the sample from the same depth at which the earlier tests showed marked results in the content of potassium chloride, was any considerable quantity of potash salts again found, but the quantity found was approximately only one-third of that shown in the earlier sample. The results seem, therefore, to indicate the presence of a potash-bearing layer, bed or stratum approximately 2,200 feet below the surface in the well.

ALUNITE AS A SOURCE OF POTASH SALTS.

COMPOSITION AS MINERAL.

The mineral alunite is a hydrous sulphate of potassium and aluminum with the symbol $K_2O \cdot 3Al_2O_3 \cdot 4SO_3 \cdot 6H_2O$. Theoretically it contains 11.4 per cent K_2O , 37 per cent Al_2O_3 , 38.6 per cent SO_3 and 13 per cent water. The composition of alunite found at Marysvale, Utah, a locality at which the mineral occurs on a considerable scale, as will be seen from the table of analyses that follow, is very close to the composition of the pure mineral as given above:

ANALYSES OF ALUNITE FROM DEPOSIT NEAR MARYSVALE, UTAH.

	18	19	Dana
Al ₂ O ₃	37.18	34.40	37.0
Fe ₂ O ₃	Trace	Trace	
SO ₃	38.34	36.54	38.6
P ₂ O ₅	.58	.50	
K ₂ O	10.46	9.71	11.4
Na ₂ O	.33	.56	
H ₂ O+	12.90	13.08	13.0
H ₂ O—	.09	.11	
SiO ₂	.22	5.28	
	100.10	100.18	100.0

No. 18 is a selected specimen of the supposedly best material. It consists of clear pink, subtransparent, coarsely granular, crystalline rock. No. 19 is a selected specimen of a light pink, very finely granular rock of almost porcelain-like conchoidal fracture and no distinct structure.

METHOD OF RECOVERING POTASH.

Experiments conducted in the laboratory of the United States Geological Survey have shown that on igniting powdered alunite all the water and three-fourths of the sulphuric acid are driven off. When the residue is leached with water, potassium sulphate dissolves and insoluble alumina is left. The average quantity of potassium sulphate leached from the ignited mineral is 17.9 per cent of the original material used. As the coarsely crystallized alunite was found

to contain 19.4 per cent potassium sulphate, 92 per cent of the total potash present was obtained by simple ignition and subsequent leaching. According to the laboratory experiments 32.7 per cent of the ignited alunite consists of available potassium sulphate, which may be obtained by leaching and evaporation. The remaining 67.3 per cent is nearly pure alumina. Several foreign deposits of alunite have been successfully worked for the manufacture of alum.⁷

UNITED STATES GEOLOGICAL SURVEY WORK ON ALUNITE.

There have been incorporated in this chapter in past years notices of all the occurrences of alunite that have been reported and described by members of the United States Geological Survey. Occurrences thus noted are those near (1) Marysvale, Piute County, Utah; (2) at five localities in the San Cristobal quadrangle, southwestern Colorado; (3) near Bozard, Esmeralda County, southwestern Nevada; and (4) in the Palmetto mining district, 5 miles south of Patagonia, Santa Cruz County, Ariz. E. S. Larsen, who described the occurrence in the San Cristobal quadrangle, Colorado, reports the mineral also at five or six different places in the Uncompahgre quadrangle, also in southwestern Colorado.

NEW OCCURRENCE OF ALUNITE IN UTAH.

Specimens containing alunite were sent to the Survey early in 1914 from the Newton mining district, about nine miles northeast of Beaver, Beaver County, Utah, by William A. Wilson, of Salt Lake City. The material was said to have been collected from the locality known as Sheep Rocks, situated on the western flank of the same mountain range under geologic conditions similar to those of the occurrence near Marysvale.

The material sent to the Survey has been examined by B. S. Butler and found to be a mixture of the minerals alunite and quartz, there being approximately 30 to 40 per cent of the latter. It should be borne in mind that the presence of alunite in the proportion given above is based on results obtained from the examination of a single specimen. Whether further search will develop a considerable body of the mineral is entirely problematical. It is interesting, however, to note, as stated elsewhere in this report, the rather general distribution of alunitization, as this form of rock alteration may be called.

Attention on the part of the owners and others interested in these and other similar deposits should be given to the interesting results obtained in experiments with alunite as a fertilizer both in the raw and in the roasted form. These results are outlined in another part of this report.

UTILIZATION OF ALUNITE.

Though the mineral alunite, since attention has been directed to it as a possible source of potash salts and alumina, has been found to be quite widespread in oc-

⁷Butler, B. S., and Gale, H. S., Alunite, a newly discovered deposit near Marysvale, Utah; U. S. Geol. Survey Bull. 511, pp. 10-11, 1912.

currence in certain of the Western States, and has come to be recognized as a rather common form of rock alteration, the Marysvale, Utah, deposit is the only one that has been regarded as of any commercial importance up to the present time. The composition of the Marysvale mineral has already been indicated.

One of the companies interested in the occurrence near Marysvale is the Florence Mining & Milling Co. This company issued a prospectus in 1913 outlining the benefits of potash as a fertilizer and giving some concrete data on the company's holdings and alunite near Marysvale.

Certain newspaper reports regarding the future exploitation of the Marysvale deposits which have come to the Survey's attention, but which must be distinctly understood as not authenticated by it, are as follows:

Among the plans for the exploitation of the Marysvale alunite is one for the erection of a roasting and grinding plant, which is to be installed in the spring of 1914. Because of the possible injury to the forests from the fumes of the oxides of sulphur given off during the roasting of the mineral, it is thought that the plant will not be permitted in the mountains near the occurrence itself. It is probable, therefore, that it will be built near the Denver & Rio Grande station at Marysvale, at which locality the prevailing winds will carry the acid fumes into the barren foothills of the ranges east of the valley. An aerial tram is projected to convey the ore from Cottonwood Canyon to the plant.

Method of Utilizing Alunite.—A process for obtaining sulphate of potash and alumina has been devised by H. F. Chappell, and is described in patent No. 1,070,324, dated August 12, 1913. According to the specifications in this patent, sulphate of potash and aluminum oxide are obtained from natural deposits of alum stone, alum rock and alunite by heating them at a temperature of about 800° to 1000° C. until the aluminum compounds present are converted into insoluble aluminum oxide and the potassium compounds present are converted into potassium sulphate. The latter salt is then extracted by lixiviation.

KELP AS A SOURCE OF POTASH SALTS.

Private Investigations.

The utilization of kelp as a source of potash salts has been discussed in detail in this chapter in the last two years. In the report for 1911, especially, the results of private investigation and those of the Bureau of Soils were outlined. These results will not be repeated here, but the outline of the progress of the work to date and the more important results which apparently have been derived therefrom will be given.

The occurrence of potash salts in large amounts in kelp has been known for many years. The experiments of David M. Balch, on the Pacific coast kelps began early in 1905. Balch gives in the articles cited a concise description of the range, relative abundance, life habits and chemical composition of the three most important giant kelps of the Pacific coast. He also

considers their economic value and the practical methods of utilizing their products.

Investigations by the Bureau of Soils.

During the spring and summer of 1911, work on the Pacific coast kelps was begun by the Bureau of Soils of the Department of Agriculture. During that year field observations were made on Puget Sound, on the California coast from Golden Gate to Point Sur, and from Cape Conception to Point Loma. Laboratory investigations were carried out on the material collected. The work was continued during 1912, and as a result there have been prepared maps of the kelp groves covering an area of 230 square miles on the Pacific coast from Puget Sound in the United States to the Cedros Islands in Mexico. The details of the work accomplished are contained in different publications of the Bureau of Soils, which have appeared in both official and unofficial journals.

During the season 1913, work both in the field in the laboratory was done by the Bureau. Two parties were engaged in locating and determining the extent and important characteristics of the kelp along the shore line of Alaska. Another party investigated on the ground the possibilities of developing a combined fish scrap and kelp industry on Puget Sound and in Alaska. Observations were made at La Jolla and Point Firmin, Cal., and at Friday Harbor, Wash., on the life history of these algæ, especially in relation to cutting and harvesting them.

Three papers—one on the leaching of potash from freshly cut kelp,⁹ the second on the analyses of certain of the Pacific coast kelps,¹⁰ and the third on the composition of the giant kelps¹¹—appeared during 1913 or early in 1914. From the experiments of Merz and Lindemuth it is shown "that it is a matter of considerable difficulty to obtain a fair average sample of wet kelp," and also "that freshly cut kelp when immersed in seawater does not, at least at first, lose its potash content very rapidly." In a later paper by Merz¹² the conclusions arrived at by Merz and Lindemuth referred to above were corroborated.

With reference to the composition of giant kelps, Merz has found that *Nereocystis* of Alaska waters is, as respects potash content, of as great importance as an economic source of potash salts as that of the more southern waters. *Macrocystis* contains a lower percentage of potassium than does *Nereocystis*, while *Alaria* contains a decidedly lower percentage. The seaweeds *Fucus* and *Porphyra* are evidently valueless as sources of potash on an economic scale.

Another observation made in connection with Merz's work is that in every instance where stems and leaves were separately analyzed the total salt content and similarly the potash content in the stem exceeded that

⁹Jour. Ind. and Eng. Chem., vol. 1, No. 12, pp. 777-787, 1909.

¹⁰Merz, A. R., and Lindemuth, J. R., Jour. Ind. and Eng. Chem., vol. 5, No. 9, pp. 729-730, September, 1913.

¹¹Parker, E. G., and Lindemuth, J. R., Jour. Ind. and Eng. Chem., vol. 5, No. 4, pp. 287-289, April, 1913.

¹²Merz, A. R., Jour. Ind. and Eng. Chem., vol. 6, No. 1, pp. 19-20, January, 1914.

¹³Op. cit., p. 19.

in the leaves, a conclusion at variance with that previously but tentatively drawn by Cameron. It was also found that (1) the ash content is generally higher in the leaves than in the stem of the same plant, and (2) that the nitrogen content is generally larger in the laminae than in the stipe of the same plant.

The work of Parker and Lindemuth¹³ on the giant kelps has enabled them to draw the following conclusions. These kelps are the most important from an economic point of view, both from their size and from the large amount of potash salts which they contain. They occur from 30 to 200 feet in length, and in specific cases much longer, while the smaller varieties occur only from 2 to 12 feet in length. In the northern areas the commercial species are *Nereocystis leutkeana* and *Macrocystis pyrifera*; in the southern areas the commercial species are *Macrocystis pyrifera* and *Pelagophycus porar*. Other conclusions which these workers have been able to draw from their experiments are (1) that the average content in potassium chloride in the giant kelp is high; (2) that apparently no definite relation exists between the different constituents of kelp; (3) that apparently the northern kelps are richer in potassium chloride than the southern; (4) that the potash content of *Nereocystis* is greater than that of *Macrocystis*, and (5) that the iodine content of the northern and southern kelps shows no conclusive differences.

In a paper by F. K. Cameron¹⁴ on kelp and other sources of potash, the recent information regarding kelp as a source of potash is summarized up to the time of publication. From the averages of the many existing analytical data, Cameron states the following conclusions, derived in part at least from the work of his colleagues of the Bureau of Soils: (1) No definite quantitative relations exist between the different constituents of kelp; (2) the potassium content of *Nereocystis* is greater than that of *Macrocystis*; (3) the potassium content of northern kelp is higher than that of southern kelp, and (4) there is no positive difference in iodine content between northern and southern kelps. So far as results obtained are available, Cameron considers that the following conclusions also seem justified: (5) The proximity of the mouth of a fresh-water stream has no appreciable effect on the potash and nitrogen content of kelp; (6) there are no essential differences between the potash and nitrogen content of fronds and stipes (which conclusion was changed by the subsequent work of Merz already referred to), and (7) there are no essential differences in the potash and nitrogen content of old and young plants, but further data on this point are desirable, as well as on the possible variations in the potash content with the season.

COMMERCIAL UTILIZATION OF KELP.

Since interest has been aroused in kelp as a source of potash salts, several companies have been formed

having in view its commercial exploitation either in the dried form as a fertilizer or for the potash salts and the other valuable ingredients, such as iodine, which it contains. The names of 11 companies formed ostensibly to engage in the kelp industry have been brought to the attention of the Survey during the last year. In geographical distribution these companies are located in the vicinity of Puget Sound, with headquarters chiefly at Seattle, and on the southern California coast near Long Beach, Los Angeles and San Diego. Two of these companies were mentioned in this report for 1912.

The American Potash Co., with offices at Los Angeles, Cal., plans to utilize the kelp in the vicinity of Long Beach. This company was formed by the merging of two other companies, one of which was the Coronado Chemical Co., of San Diego and Cardiff. It is stated that work will begin early in 1914 on the manufacture of potash and other by-products from kelp at a plant to be built at Long Beach. The plant is to be erected on the unit system, and construction work on it began early in 1913. The work of manufacturing potash will begin on the completion of the new buildings that are expected to be finished about April 1, 1914.

The Pacific Products Co., of San Pedro, Cal., with a capital of \$100,000, is reported to have a factory site on the California coast opposite the kelp grove outside of Point Firmin.

The Pacific Products Co., of Seattle, Wash., capitalized at \$125,000, will build a factory for the manufacture of fertilizer materials and by-products from fish and kelp at Port Townsend, Wash. Several beds of kelp have been optioned at the head of Puget Sound, where a large quantity of seaweed will be harvested each year and transferred to the factory at Port Townsend. This company will also make a business of obtaining dogfish and of utilizing the offal from the fish canneries in the vicinity. The first unit of the plant for converting kelp and dogfish into fertilizer material was reported completed in July, 1913.

The Pacific Kelp Mulch Co. is located at Terminal Island, one mile east of East San Pedro, on the San Pedro, Los Angeles & Salt Lake Railroad. The company has been gathering kelp from the ocean during the last two years and disposing of it to the farmers and fruit growers as a fertilizer. The company has developed a machine which harvests the kelp rapidly and on a large scale. The kelp is cut from 4 to 6 feet under water, and care is taken not to disturb the roots of the growing plants. It is loaded on a barge and brought to the boat landing of the plant. Here it is pitchforked from the barge on a belt conveyer, which conveys it to the cutter, being subjected during the passage to a steaming process which is practically instantaneous and which, it is asserted, removes all the adhering common salt (NaCl), but none of the potash salts. The cutter chops it into pieces 6 to 8 inches long, that is, of a length to be conveniently handled with a

¹³Jour. Ind. and Eng. Chem., vol. 5, No. 4, pp. 287-289, April, 1913.

¹⁴Franklin Inst. Jour., vol. 176, No. 4, pp. 347-353, October, 1913.

manure fork or to be harrowed under the soil after being spread. From the cutter the kelp falls into wagons or to the floor. It is then carted to the railroad and dumped into freight cars and shipped to the centers of consumption. This company has the distinction of being the first to harvest and market kelp on a commercial scale.

The material is said to have many advantages as a fertilizer, and these are explained in a small pamphlet which has been issued by the company.

The other companies whose names have come to the Survey as proposing to engage in the production of kelp on a commercial scale are the following:

Ocean Products Co., Seattle, Wash.

North Pacific Kelp Potash Co., Seattle, Wash.

Pacific Coast Kelp Potash Co., Seattle, Wash.

Puget Sound Kelp Potash Co., Seattle, Wash.

Aquatic Products Co., Seattle, Wash.

Kelp Products Co., San Francisco, Cal.

Mexican Kelp Fertilizer Co., Los Angeles, Cal.

The Survey has no first-hand knowledge of the activities of these companies.

ALUNITE AND KELP AS FERTILIZERS.

In experiments with alunite as a source of potash, Waggaman¹⁵ found that a large quantity of water is required to free the ignited residue entirely from soluble salts, and that the subsequent evaporation is tedious and expensive. He suggested, therefore, that it might be more economical to use ignited alunite directly as a fertilizer than first to leach the residue for the potassium sulphate contained in it.

Experiments have been made by Skinner and Jackson¹⁶ with alunite as a fertilizer in which both the raw and the ignited mineral have been used. The sample of raw alunite containing 10 per cent potash (K_2O) was finely ground, as was also the sample of the ignited mineral which contained 14.7 per cent potash. These minerals were applied to the soil in such quantities as would furnish 25, 50, 100, 200 and 500 pounds of potash to the acre. Experiments with kelp were also tried, the material used being in the dried state and containing 19.8 per cent potash. This likewise was applied to the soil in such quantities as to furnish 25, 50, 100, 200 and 500 pounds of potash per acre. Check experiments were also made containing equivalent quantities of potash in the forms of the sulphate and the chloride, while in still another experiment no fertilizer was used. This last was in the nature of a control experiment.

The cultural methods employed and the results obtained from these experiments are as follows:

The soil was weighed into pans, three pounds to each pan. The soil in one pan received no fertilizer and was used as a control. To each of the other pans

the fertilizer to be tested was added. To the different pans of soil were added raw alunite, ignited alunite, kelp, potassium sulphate and potassium chloride, each in quantities of 25, 50, 100, 200 and 500 pounds of potash (K_2O) per acre, based on an acre half-foot of soil weighing 2,000,000 pounds.

The soil used in the first experiment was the Carlington loam—a soil which is known to respond well to potash fertilizers in field practice. The soil was treated with the various fertilizers in pans on October 22d, was well mixed by sifting, and was potted October 28th. Three pots, each holding about a pound of soil, were used for each treatment. Six wheat plants were planted in each pot. The plants grew until November 29th. At the end of the experiment the plants were cut and the green weights recorded. The results of the test are given in the accompanying table. The last column gives the relative growth of the different treatments. The growth of the check or control is taken as 100. The second column gives the green weights of the three cultures in each treatment.

EFFECT OF ALUNITE AND KELP AS COMPARED WITH THAT OF POTASSIUM SULPHATE AND POTASSIUM CHLORIDE ON GROWTH.

Treatment.	Quantity of K_2O Added per Acre. Pounds.	Green Weight. Grams.	Relative Growth. Per cent.
Soil untreated	...	3.35	100
Soil + raw alunite	25	3.70	110
	50	4.00	119
	100	4.02	120
	200	3.77	112
	500	3.72	111
Soil + ignited alunite.....	25	4.58	136
	50	4.77	142
	100	4.80	143
	200	4.80	143
	500	4.53	135
Soil + kelp.....	25	3.93	117
	50	4.67	139
	100	4.80	143
	200	4.40	131
	500	4.30	128
Soil + K_2SO_4	25	4.27	127
	50	4.33	129
	100	5.12	152
	200	4.52	135
	500	4.90	146
Soil + KCl	25	4.40	131
	50	4.33	129
	100	4.50	134
	200	4.37	130
	500	4.40	131

By examination of the table it is seen that each of the potash fertilizers produced an increased growth over the untreated soil. The raw alunite used in amounts of 25 to 500 pounds of K_2O per acre increased growth from 10 to 20 per cent. The best results were secured with 50 to 100 pounds of potash (K_2O) per acre. The average increase over the untreated soil of the five amounts was 14 per cent. When the growth is compared with that produced by the ignited alunite it is seen that this caused larger growth with each amount used than did the raw alunite. The increase in growth with ignited alunite over the untreated soil varied from 35 to 43 per cent, the average increase being 40 per cent. The growth with the raw alunite was not so good as with similar amounts of potash as potassium sulphate and potassium chloride.

¹⁵Waggaman, W. H., U. S. Dept. Agr. Bur. Soils Circ. 70, 4 pp., July 31, 1912.

¹⁶Skinner, J. J., and Jackson, A. M., Alunite and kelp as potash fertilizers: U. S. Dept. Agr. Bur. Soils Circ. 76, 5 pp., April 10, 1913.

The average increase with potassium sulphate was 38 per cent, and with potassium chloride was 31 per cent. The effect of ignited alunite was about the same as that of potassium sulphate, and greater than that of the potassium chloride.

Kelp produced a considerable increase in growth over the untreated soil. The increase varied with the different amounts, from 17 to 43 per cent. The average increase over the untreated soil was 31 per cent. The increased growth was about the same as that produced by potassium chloride, and was slightly less than that resulting from the use of potassium sulphate. It should be here noted that the potash in the kelp is in the form of the chloride.

Another experiment was made to test the effect of these potash compounds, using this time a different soil. Otherwise the details of the experiment were the same as in the first test. The soil used in this test was the Volusia silt loam. The plants grew from November 19th to December 21st. Three pots were used for each treatment. The results are given in the table which follows:

EFFECT OF ALUNITE AND KELP AS COMPARED WITH THAT OF POTASSIUM SULPHATE AND POTASSIUM CHLORIDE ON GROWTH.

Treatment.	Quantity of K ₂ O Added per Acre. Pounds.	Green Weight. Grams.	Relative Growth. Per cent.
Soil untreated	...	2.84	100
Soil + raw alunite	25	3.35	118
	50	3.40	120
	100	3.36	118
	200	3.36	118
	500	3.02	106
Soil + ignited alunite.....	25	3.54	124
	50	3.70	130
	100	3.70	130
	200	3.90	137
	500	3.94	136
Soil + kelp.....	25	3.24	114
	50	3.54	124
	100	3.59	127
	200	3.60	127
	500	3.45	121
Soil + K ₂ SO ₄	25	3.08	108
	50	3.62	127
	100	3.87	136
	200	3.68	129
	500	5.54	124
Soil + KCl.....	25	3.04	108
	50	3.50	123
	100	3.50	123
	200	3.74	131
	502	3.60	127

Each of these potash fertilizers had a beneficial effect on Volusia silt loam. The raw alunite again produced less increased growth than the ignited alunite. This was true with each amount of the substances used. The raw alunite was not as effective as potassium sulphate and potassium chloride. However, the ignited alunite was more effective. The average for the raw alunite was 16 per cent, for the ignited alunite 31 per cent, for potassium sulphate 25 per cent, and for potassium chloride 22 per cent.

As in the first experiment, kelp again produced considerable increase in growth. The effectiveness in producing plant growth was practically the same as that of potassium sulphate and potassium chloride. Kelp gave as an average 23 per cent increase in

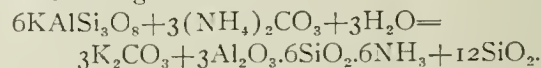
growth, potassium sulphate 25 per cent, and potassium chloride 22 per cent increase. In addition to the amount of potash added to the soil by the kelp, it contains a small amount of nitrogen and phosphorus, which should be effective in the soil. From these two experiments it seems that the dried kelp and ignited alunite are about as effective potash fertilizers as the salts, potassium sulphate and potassium chloride.

POTASH SALTS FROM THE SILICATE ROCKS.

If the interest in the problem of the derivation of potash salts from the silicate rocks is to be judged from the number of processes which have been devised and patented, then the year 1913 showed no abatement in this interest. Several patents have been secured covering such processes, and a few articles on the subject have also appeared in the scientific literature. The more important of these processes are briefly reviewed below.

Process of Morse and Sargent.—H. W. Morse and G. W. Sargent (patent No. 1,041,327, dated October 15, 1912) have invented a process in which feldspar is subjected at an elevated temperature, first, to the action of sulphate of lime (gypsum), and, second, to that of an alkaline chloride such as common salt or to a chloride of an alkaline earth metal as calcium chloride. There are produced oxides of sulphur, a soluble compound of potassium and residual material which may be converted into Portland cement. According to the claims of the patentees, it is the production of the oxides of sulphur and the cement material in connection with that of the soluble potassium compound that makes possible the economical manufacture of the latter.

Process of Gelléri.—In the process of S. Gelléri (patent No. 1,058,686, dated April 8, 1913) silicates are burned with lime or with an oxide or carbonate of an alkaline earth metal or magnesium for the purpose of decomposing the silicate and obtaining potash and cement clinker. After the silicates have been decomposed in this manner a large portion of the alkalis in them is still not in a condition whereby it may be leached with water. According to Gelléri's process this disadvantage is overcome by subjecting the silicates in a closed chamber to the action of ammonium carbonate vapor under pressure either after they have been burned with the oxides or carbonates of the alkaline earth metals or without this preliminary burning. By so doing the silicates are completely decomposed, and the whole of the alkali metal may be obtained in the form of an alkali carbonate by leaching with water. The decomposition takes place according to the following reaction:



This process has the advantage that the whole of the ammonia in the ammonium carbonate is liberated, and, after the reaction is completed, the free ammonia may be used over again to make ammonium carbonate. This is most economically accomplished by saturating

the ammonia with carbon dioxide from the furnace in which the silicates are burned with limestone. In order that a separate furnace may not be necessary to heat the silicates with ammonium carbonate, the furnace gases coming from the burning kiln may be used.

If the silicates have been burned with lime before being treated with ammonium carbonate, they contain all the constituents corresponding with the composition of Portland cement, so that it is possible to burn the silicates which have been decomposed and freed from alkalis to Portland cement by heating them again.

Process of Hart.—According to E. Hart (patent No. 1,062,278, dated May 20, 1913), when feldspar or similar rock is mixed with potassium or sodium sulphate and carbon and heated to fusion in a furnace, there is formed a soluble glass consisting of a potassium or sodium aluminum silicate. This glass may readily be decomposed by the addition of a suitable acid like sulphuric, which forms practically pure silica and a solution from which potassium and aluminum may be obtained in the form of common potash alum, leaving a mother liquor which contains sulphates of potassium, sodium or aluminum, some free sulphuric acid and other sulphates formed by the action of the acid.

The mother liquor is evaporated to dryness and fused with a suitable amount of carbon. The residue consists chiefly of aluminate of soda or potash, or both, or of one or more of these substances, together with alumina. If water be added to the residue, the aluminate of soda or potash will be largely dissolved, and there will be left an insoluble residue consisting chiefly of sulphide of iron, with possibly some alumina. From the solution of the aluminate of soda or potash alumina may be obtained by the usual methods.

Process of Bassett.—An invention by H. P. Bassett (patent No. 1,072,686, dated September 9, 1913) relates to the treatment of feldspar or feldspathic rock to obtain potash, and has particular reference to a process of not only obtaining potash salts from feldspar or feldspathic rock, but also of obtaining, in the form of a by-product, material which is adapted for use in manufacturing pottery.

Bassett has found that potash may be economically and satisfactorily obtained from feldspar by treatment with salt alone, and that the potash salts and by-products of the reaction may be obtained in relatively pure form. In practice he adds to disintegrated and preferably finely ground feldspar or feldspar-bearing rock, about one-half its weight of sodium chloride. The mixture is next heated to a yellow heat, preferably from 800° to 900° C., in the presence of air, for about one to two hours. The mass is then dumped while still hot into a vat of water in the proportion of about two to five parts by weight of water to one part of the fused mass. The mass is then leached with water, and the potash and sodium salts are obtained in any desired manner, preferably by evaporation of the solution to dryness. The potassium and sodium salts

are later separated, for example, by crystallization. The leached residue, which corresponds in composition closely with that of the feldspathic rock, except that the potassium is replaced by sodium, and that any iron present in the original rock will have been volatilized as iron chloride, and thus removed, is then dried and ground, the resulting product being a white mass that may be used for pottery or other purposes, such as a paper filler or enamel ware. The feldspar or feldspar-bearing rock may be ground to any desired fineness before treatment, but preferably not less than 40 mesh; finer grinding than 100 mesh is unnecessary. The leached residue is dried and ground and is then ready for use.

Process of Cowles.—Early in 1913, A. H. Cowles¹⁷ described the results of certain experiments having to do with the extraction of potash alum and other soluble potash salts from the insoluble potash silicates. Cowles' experiments differ from those which have been described in that he mixes rock phosphate with the feldspar, thus incorporating a second fertilizer element into the resulting mixtures.

In the first experiments potash feldspar was ground with rock phosphate in such proportion as to furnish two molecular weights of lime to each molecular weight of silica in the feldspar. The mixture was heated to a sintering temperature of about 1000° C., and the resulting product was leached with sulphuric acid. The resulting yield was practically 100 per cent. The products formed were insoluble dicalcium silicate, soluble potash alum and orthophosphoric acid.

In the subsequent experiments less acid was used, and the results of the leaching gave a product containing all the potash and alumina in the feldspar, but only part of the phosphoric acid. Duplicate experiments have been carried out in which hydrochloric instead of sulphuric acid was used. The solutions in the two cases gave either potash alum or the double chloride of potash and aluminum together with the phosphoric acid in the rock phosphate used in the experiment. Any iron present in the raw material used goes into solution with the aluminum and potash. From either the potash alum or the double chloride of aluminum and potash the opportunities for securing alumina are good. If the potash alum is heated to a dull red heat, the aluminum sulphate breaks down into alumina (Al_2O_3) and sulphuric acid (SO_3) and the potash sulphate may be leached away. If the double chloride of aluminum and potash is treated with water at a low temperature, hydrochloric acid is given off with the formation of alumina. The potassium chloride remains and may be leached away.

PRIVATE ENTERPRISE IN CONNECTION WITH THE EXTRACTION OF POTASH SALTS FROM THE SILICATES.

The Spar Chemical Co., with headquarters at Baltimore, Md., has done some experimental work on the

¹⁷Paper read at the joint meeting of the American Electrochemical Society, the American Chemical Society, and the Society of Chemical Industry, New York, Feb. 7, 1913; Jour. Ind. and Eng. Chem., Apr., 1913, pp. 331-335.

extraction of potash salts from the silicate rocks at a plant located at Curtis Bay, on the outskirts of the city. It is understood that the products are made according to the Thompson method, which is briefly outlined as follows:

Thompson's process is described in patent No. 995,105, dated June 13, 1911. It consists first of grinding feldspar rock so that it will pass through a 100-mesh sieve. The powdered rock is then mixed with an acid alkali sulphate and an alkali chloride, preferably acid sodium sulphate and sodium chloride, respectively. The proportions of the materials used are: Feldspar rock, 5 parts by weight; acid sodium sulphate, 5 parts by weight; sodium chloride, 1.8 parts by weight. This mixture is heated from one to two hours at a bright red heat, and becomes thereby partly fused. The mass is then allowed to cool, is ground again, and is leached with water, which removes a mixture of sulphates of

potassium and sodium. These salts are then separated by crystallization. The reactions are believed to be as follows: (a) The sodium acid sulphate reacts with the sodium chloride to produce hydrochloric acid gas and normal sodium sulphate; (b) the hydrochloric acid gas at the high temperature employed reacts on the feldspar, producing potassium chloride; (c) the potassium chloride is in turn acted upon by more of the acid sodium sulphate, producing hydrochloric acid gas and potassium sulphate.

The yield of potash is ordinarily from 80 to 90 per cent of the potash in the rock. For the best results the temperature must be controlled within rather narrow limits.

SHIPMENTS FROM GERMAN POTASH MINES.

From data obtained from reliable sources the following table, showing the shipments of potash salts and potash fertilizers in metric tons from the German pot-

TABLE II—EXPORTS OF GERMAN POTASH SALTS IN 1911 AND 1912.

	1911		1912	
	Total.	To United States.	Total.	To United States.
Potash salts.				
Muriate of potash.....	329,751	229,431	286,528	190,775
Sulphate of potassium.....	109,529	56,893	85,452	35,366
Sulphate of potassium-magnesium.....	*282,574	*143,775	48,540	14,172
Carnallite with at least 9% and less than 12% K ₂ O....			6,853	†
Raw potash salts with from 12 to 15% K ₂ O.....	1,167,972†		852,984	461,279
Raw potash salts with more than 15% and less than 20% K ₂ O.....			35,529	29,533
Manure salts, including potash salts with 38% K ₂ O.....			373,665	149,907
Abraum salts, Stassfurter salts, etc.....			31,322	9,578
Total.....	1,889,826		1,720,837	890,610

*Includes manure salts.

†Not stated.

‡Only the total exports of the last five salts for the year 1911 are given in the new statistics, and the shipments to the United States during that year are not specified.

TABLE III—POTASH SALTS IMPORTED INTO UNITED STATES FOR THE CALENDAR YEARS 1910-1913, IN POUNDS.*

	1910		1911		1912		1913	
	Quantity.	Value.	Quantity.	Value.	Quantity.	Value.	Quantity.	Value.
Potash: Carbonate of.....	18,963,619	\$ 616,371	20,332,990	\$ 636,356	20,530,846	\$ 658,343	21,436,533	\$ 652,635
Caustic, not including ref.	8,304,696	346,388	7,069,837	287,116	9,578,437	365,860	8,590,120	335,147
Cyanide of.....			\$2,114,684	\$316,027	1,138,569	169,627	1,023,167	143,999
Chloride of.....	381,873,875	5,252,373	509,119,193	7,651,681	482,265,665	7,229,109	478,826,857	7,120,055
Nitrate of, or saltpeter, crude	11,496,904	333,854	7,945,747	265,061	7,315,531	216,492	9,876,910	262,575
Sulphate of.....	86,162,874	1,426,975	121,039,192	2,227,820	97,161,010	1,769,676	88,565,073	1,633,114
All other‡.....	3,389,684	387,662	4,583,940	442,042	3,509,444	316,989	6,114,748	554,637
Total.....	510,191,652	\$8,363,623	672,205,583	\$11,826,106	621,499,502	\$10,726,096	614,433,408	\$10,702,162

*This table is based on total imports for the calendar year, not, as some tables, on imports for consumption for the calendar year.

†Included in "All other chemicals" prior to July 1, 1911.

‡Included in "All other chemicals" prior to July 1, 1909.

§Figures cover period since July 1.

TABLE IV—POTASH SALTS IMPORTED FOR CONSUMPTION INTO THE UNITED STATES FOR THE CALENDAR YEARS 1911-1913, IN POUNDS.

	1911		1912		1913	
	Quantity.	Value.	Quantity.	Value.	Quantity.	Value.
Potash: Carbonate of, crude.....	8,604,855	\$ 255,096	7,625,382	\$ 234,868	9,715,878	\$ 272,973
Caustic, not including refined.....	7,072,093	287,997	9,690,494	370,506	8,648,753	*342,056
Cyanide of.....	2,649,040	294,141	726,659	109,434	1,395,987	205,037
Chloride of.....	506,570,661	7,651,693	482,529,396	7,229,121	475,261,595	7,075,745
Nitrate of, saltpeter, crude.....	7,944,757	265,061	6,511,208	202,899	9,652,366	261,078
Sulphate of.....	121,710,568	2,240,631	98,237,150	1,783,846	88,698,193	1,677,429
All other.....	15,570,411	689,662	16,858,875	761,611	19,067,144	959,595
Total.....	670,122,385	\$11,783,381	622,179,164	\$10,692,285	612,439,916	\$10,793,913

*Including refined.

ash mines, for native and foreign consumption, during the last two years, has been compiled:

SHIPMENTS OF POTASH SALTS FROM GERMAN MINES IN 1911 AND 1912.

Potash Salts.	1911	1912.
Muriate of potash.....	443,357	471,435
Sulphate of potassium.....	110,123	115,728
Magnesium, 18% K ₂ O.....	49,014	55,987
Magnesium, 40% K ₂ O.....	144	173
Manure salts:		
Minimum, 38% K ₂ O.....	38,620	48,059
Minimum, 20% K ₂ O.....	169,812	174,867
Minimum, 30% K ₂ O.....	57,502	64,514
Minimum, 40% K ₂ O.....	379,790	483,877
Kainit and sylvinite.....	3,312,632	3,251,003
Carnallite, etc.....	80,660	70,162
Total.....	4,641,654	4,736,105

Changes have been made in the method of prepar-

SURFACE COMBUSTION.

An interesting discussion of surface combustion was given by Prof. W. A. Bone in the first and second Howard lectures delivered recently before the Royal Society of Arts, London, England. In his first lecture Prof. Bone reviewed the consideration which had convinced him of the possibility of realizing in practically applicable forms, and by means of common refractory materials, the basic conception of flameless incandescent surface combustion. In the second lecture he describes the experimental development of two new processes embodying this principle.

The lectures were reprinted in the American Gas

TABLE V.—FERTILIZERS IMPORTED AND ENTERED FOR CONSUMPTION IN THE UNITED STATES, 1909-1913, IN LONG TONS.

Fertilizer.	1909		1910		1911		1912		1913	
	Quantity.	Value.	Quantity.	Value.	Quantity.	Value.	Quantity.	Value.	Quantity.	Value.
Apatite.....	2,925	\$ 19,013			20	\$ 300	100	\$ 1,400	2,962	\$ 22,471
Bone dust or animal carbon, and bone ash, fit only for fertilizing purposes.....	29,035	685,291	48,979	\$1,140,476	36,856	943,472	117,717	878,686	35,012	851,136
Calcium cyanamid or lime nitrogen.....	*	*	3,540	177,552	5,292	292,496	9,311	493,519	26,729	1,410,248
Guano.....	44,197	772,674	33,565	667,870	36,869	774,315	19,128	329,624	16,674	518,429
Kainit.....	163,943	854,998	582,197	2,798,198	563,957	2,748,140	511,976	2,386,362	465,336	2,201,730
Manure salts, including double manure salts.....	†52,958	601,804	147,242	1,013,000	159,796	1,660,040	171,757	1,797,057	223,687	2,245,509
Phosphates, crude.....	9,983	99,060	21,706	23,040	16,153	157,394	23,821	231,255	17,121	124,815
Slag, basic, ground or unground	690	5,880	10,774	93,650	12,622	87,994	12,596	114,300	13,186	130,455
All other substances used only for manure.....	184,850	2,879,845	195,991	3,394,279	197,810	4,098,321	127,932	2,660,887	154,729	3,314,460
Total.....	488,581	\$5,918,565	1,043,994	\$9,520,074	1,029,375	\$10,762,472	999,338	\$8,893,090	955,436	\$10,819,253

*Not separately classified.

†From Aug. 5 to Dec. 31.

ing the statistics for 1912 so as to preclude comparison in all cases between shipments of that year with 1911. Table II shows the exports of German potash salts for 1911 and 1912 and the amount shipped to the United States, in metric tons, with comparisons where possible.

CONSUMPTION OF POTASH SALTS IN THE UNITED STATES.

Table III gives the total imports of potash salts in pounds for the years 1910 to 1913, inclusive.

For comparison Table IV is added. This gives the potash salts imported for consumption into the United States during the calendar years 1911, 1912 and 1913, in pounds.

It will be observed that there was a slight decrease in both quantity and value of potash salts imported in 1913 as compared with 1912. The quantities of carbonate, cyanide, nitrate and "all other salts" of potassium increased, while the quantity of caustic potash, chloride and sulphate diminished. The results, especially in the case of the two latter salts, are of interest, for among the potassium salts imported it is presumably these two that enter most largely into the commercial fertilizer industry.

The importation of potash salts given in these tables is only a part of that entering the United States from Germany. To it should be added the importation of kainit and manure salts. The quantity and value of imported fertilizers, including kainit and manure salts, are given in detail in Table V. It indicates a growing and prosperous industry.

Light Journal, to which we are indebted for the matter that follows:

During his researches upon flame, Sir Humphrey Davy discovered, in 1817, that combustible gases will combine slowly with oxygen at temperatures below the actual ignition point. Thus he wrote: "I made various experiments on explosives, by passing mixtures of hydrogen and oxygen through heated tubes. In the beginning of one of these trials, in which the heat was much below redness, steam appeared to be formed without any combustion. This led me to expose mixtures of oxygen and hydrogen in tubes, in which they were confined by fluid fusible metal, to heat; and I found that, by carefully applying heat between the boiling point of mercury, which is not sufficient, and a heat approaching the greatest heat that can be given without making glass luminous in darkness, the combination was effected without any violence and without any light." This led him to try whether temperature of these slow combinations being lower than required to produce flame, might yet be high enough to make solid bodies incandescent. Or, to put the question differently, whether, seeing that the temperatures of flames far exceed those at which solids become incandescent, a metallic wire can be maintained at incandescence by the combustion of gases at its surface without actual flame. He thereupon tried the effect of introducing a warm platinum wire into a jar containing a mixture of coal-gas and air rendered non explosive by an excess of the combustible constituents. The wire immediately became

¹⁰Daily Cons. and Trade Repts., June 18, 1913.

red-hot, and continued so until nearly all of the oxygen disappeared.

He effected similar results with mixtures of air and various single combustible gases (ethylene, carbonic oxide, and hydrogen), all of which are found capable of making a warm platinum wire glow, the effect of which being more intense in hydrogen than in ethylene, and more in ethylene than carbonic oxide. He succeeded in repeating the phenomena with palladium wire, but failed with silver, gold, iron, copper, and zinc. He says, that Sementini, presented him in 1819, with a lamp, "in which alcohol burnt without flame, by means of fine coils of silver wire." Davy suggested an electro-chemical explanation of the phenomena.

Although Davy was the first chemist to observe and record an instance of surface combustion, he was far from recognizing that *all* incandescent surfaces are equally capable of effecting it, which, we shall see later, is our modern conception of the phenomenon. He believed that a *metal* surface was necessary, preferably a metal of the platinum group.

During the twenty years following Davy's discovery, several distinguished chemists, investigated the matter. Dulong and Thénard found that the power of inducing the slow combination of gases is possessed in varying degrees by all solids, dependent upon their specific characters, physical texture, and temperature. Thus whereas finely divided platinum can bring about the combination of hydrogen and oxygen at the ordinary temperature, gold and silver require a temperature of 160° to 250° C.; whilst non-metallic substances, such as charcoal, pumice-stone, porcelain, rock crystal, and broken glass, do not become active until 350° C. No experiments were made at that time with these substances in a state of incandescence, the observations being confined to inducing of slow combustion at low temperatures. Other chemists confined their attention to metals of the platinum group, and in 1825 Dr. Henry found that when a platinum ball was immersed in a mixture of equal volumes of electrolytic gas ($2\text{H}_2 + \text{O}_2$) and ethylene, the hydrogen alone was burnt, none of the hydrocarbon disappearing unless the original mixture contained a much larger proportion of oxygen. This new observation, viewed in the light of Graham's subsequent researches upon the occlusion of hydrogen by metals, led to the idea, first put forward by the Italian physicist, Fusinieri, that the power possessed by a metal of inducing combustion depends upon a condensation or occlusion of the combustible gas (hydrogen particularly) at the surface, whereby it is rendered more than ordinarily active by association with the surface. He did not think that the oxygen of a combustible mixture was similarly affected by the surface.

The mechanism of induced slow surface combustion formed the subject of a celebrated controversy between Faraday and De la Rive in 1834-5. De la Rive held the view that it consists in a series of rapidly

alternating oxidations and reductions of the surface. Faraday, on the other hand, contended that the function of the surface is to condense both the oxygen and the combustible gas, thus producing in the surface layers a condition comparable to that of high pressure. But, owing to lack of crucial experimental data, no satisfactory theory of the process could be evolved. In 1836 interest in the subject suddenly dropped, and was not revived for more than half a century.

Meanwhile, the researches of Deville upon the dissociation of steam and carbon dioxide at high temperatures, in which he had employed incandescent surfaces, had begotten the wholly mistaken notion that because such surfaces promote dissociation they must necessarily hinder combustion, and therefore that in furnace design and construction the contact of burning gases with hot surfaces should be avoided. The late Frederick Siemens strongly upheld this view, and such was the weight of his authority in all matters relating to large-scale heating operations that his dictum was accepted without question by technical men for a generation. Seeing that Siemens's views exercised such an enormous influence upon contemporary thought and practice, it may be of interest if we consider them at close quarters. He was of the opinion that, inasmuch as "a flame consists of a chemically excited mixture of gases, whose particles are in violent motion . . . it follows that any solid substance brought into contact with gases thus agitated must necessarily have an impending effect on their motion . . . ; in the immediate neighborhood of such surfaces the combustion of the gases will cease altogether, because the attractive influence of the surfaces will entirely prevent their motion." Moreover, in referring to the influence of dissociation, he pointed out that Deville and others had made use of small vessels of special material, and that the results depended very much upon the various kinds of surfaces employed, which by some peculiar influence upon the surrounding gaseous medium had directly caused the dissociation effected. Hence, he concluded "that solid substances have a twofold influence on combustion, because they interfere with the rapid motion of the gases necessary for combustion; and, in the second place, they cause dissociation . . . and by doing so, of course, a great amount of heat is lost." And, further, that "complete combustion is impossible whenever live or active flame is allowed to come into contact with any solid surface."

No one has greater admiration than myself for the scientific work of Siemens, and the benefits which have resulted from his teachings as a whole; but, in the interests of scientific truth and technical progress, I must point out that he was wrong, and misled others, in his conception of the influence of surfaces upon combustion. It is, of course, true that a *cold* surface thrust into a flame will cool the layers of combining gases in its immediate vicinity below the ignition temperature, and so prevent the completion of combus-

tion; but this does not apply to a *hot* or incandescent surface, which undoubtedly accelerates combustion. If an incandescent surface accelerates the dissociation of steam, it must also accelerate the combination of hydrogen and oxygen. Moreover, Siemens never appeared to have contemplated the possibility of a high temperature *flameless* combustion, much less that such combustion, if realizable, will be a faster process than ordinary *flame* combustion.

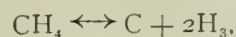
The late Thomas Fletcher, who did so much in the direction of developing the uses of gas in small-scale operations, seems to have arrived at a clearer conception than any of his contemporaries of the influence of surfaces in combustion. In a lecture at the Manchester Technical School in 1887, entitled "Some Curious Flames," he demonstrated the possibility of realizing a flameless incandescent surface combustion in contact with metals other than those of the platinum group. He said, "I will now dispense with flame altogether, and show you the same quantity of gas and air burning as before, but in the most perfect form, the combination taking place on the surface of the substance to be heated without any flame. To show this so that all can see, the mixture of gas and air is directed onto a large ball of iron wire, flame being used at first to heat the wire to the necessary temperature to continue the combustion. By stopping the gas supply for an instant the flame is extinguished, and the combustion is now continued without any flame, but with an enormous increase in the heat obtained. This invisible or flameless combustion is only possible under certain conditions; and one essential point is that the combustible mixture shall come into absolute contact with a substance at a high temperature which is capable of absorbing the heat as it is generated. . . . In the absence of a solid substance at a high temperature, it is impossible to cause combustion without flame; and when a flame is used it is also impossible to make it touch a cold surface."

Circumstances during the "nineties" directed the attention of chemists again to the possible influence of hot surfaces upon gaseous reactions. For example, the persistent attempts of the late Victor Meyer and others to determine accurately the ignition temperatures of explosive mixtures were largely thwarted by irregularities which could only be attributed to the action of the hot walls of the containing vessels; and experiments by other workers upon the velocities of chemical changes in gaseous systems led to results difficult to understand, except on the supposition of the intervention of some surface action. Thus, for example, results obtained by Bodenstein in 1899 for the velocity of the interaction of hydrogen and oxygen in porcelain vessels at temperatures between 482° and 689° C. were obviously at variance with the supposition that the gases were combining *homogeneously* throughout the whole volume, and it was in trying to find some explanation of the curious irregularities re-

vealed by a close study of his work that I first became convinced of the supreme importance of the "surface factor" in gaseous reactions. And a perusal of the earlier literature, and especially the experiments of Dulong and Thénard, led me, in 1902, to undertake a systematic experimental investigation of the whole subject.

It is now generally recognized by chemists that all hot surfaces have an accelerating influence upon chemical change in gaseous systems; or, in other words, that if at any temperature a gaseous system A tends to pass over into another system B, contact with a solid at that temperature will accelerate the process. Many examples in proof of this could be quoted, of which I may mention two as coming within my own experience:

1. At high temperatures methane decomposes directly into its elements, according to the reversible equation:



and experiments in which the gas was heated in porcelain tubes to various constant temperatures, between 800° and 1150° C., proved that the change is entirely a surface phenomenon; the gas decomposed only where it was in contact with the walls of the tube, and not throughout its main mass. Packing the tube with fragments of quicklime immensely increased the rate of decomposition. Thus, in two experiments at 1000° C., in the first, without any packing and only the hot walls of the tube exposed to the gas, about 20 per cent of the gas was decomposed in 25 minutes; in the second, with a packed tube, 96 per cent disappeared in the same time. In fact, the packing of the tube had a much greater accelerating influence than raising the temperature from 1000° to 1150° without the packing.

2. If a mixture of hydrogen and oxygen in their combining proportions (electrolytic gas) be maintained in an enclosure with smooth glass walls at a temperature of, say, 450° C., there would certainly be a tendency to form steam, but the rate of change would be negligibly small. If, however, there be brought into the system some porous solid material at the same temperature, so that a large surface is exposed to the gases, the rate of change would at once be rapidly accelerated in the layer of gas immediately in contact with the hot surface. Steam, the product, would diffuse outwards from the surface, and the supplies of hydrogen and oxygen at the surface would be renewed by diffusion inwards. This combustion would proceed at the surface until the transformation of the original electrolytic gas into steam was complete. In the circumstances cited the rate of combustion, although now quite measurable, would probably be insufficient to cause any self-heating of the enclosure. The temperature would remain at 450° C., which is well below either the ignition temperature

of the combustible mixture or the point at which a solid would attain even incipient incandescence.

It is therefore necessary to distinguish between two possible conditions under which gaseous combustion may occur, namely (1), *Homogeneously*—that is to say, equally throughout the system as a whole, at temperatures *below* the ignition points *slowly* and *without flame*, and at temperatures *above* the ignition point—*rapidly* and *with flame*; and (2), *Heterogeneously*, or only in layers immediately in contact with a hot or incandescent surface ("surface combustion"). It is also necessary to remember that the heterogeneous surface combustion is a faster process than the normal homogeneous combustion of ordinary flames.

My own researches began with an attempt to elucidate the factors operative in the combustion of hydrogen and of carbon monoxide in contact with various hot surfaces (porous porcelain, fireclay, magnesia, platinum, gold, silver, nickel, copper and the oxides of copper, nickel and iron) at temperatures below 500° C. The experimental method consisted essentially in circulating the reacting gases at a uniform rate, in a closed system, over the particular surface under investigation, maintained at a constant temperature, provision being made for the rapid removal of the reaction product from the system, either by condensation or absorption, so that the rate of combination could be measured by observing the pressure in the apparatus at regular intervals of time. The apparatus (Fig. 1), comprised a "capacity bulb," *A* (1200° to 1500°); a furnace, *D*, in which the surface under investigation, contained in a Jena glass combustion tube, was maintained at a suitable constant temperature; an automatic Sprengel pump, *G*, which kept the gases circulating through a system at a constant speed. At

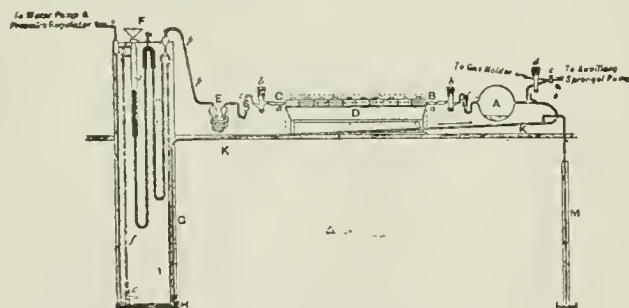


Fig. 1. Circulation Apparatus

E was inserted either a cooling worm for condensation of steam, or a series of absorption bulbs for the removal of carbonic dioxide by a solution of recrystallized baryta. *M* is a mercurial manometer for the measurement of pressure.

Although a great variety of surfaces were examined over wide ranges of temperature, these characteristic features were found to apply in nearly all cases:

1. The catalyzing power of a new surface usually increases up to a steady maximum, after which, provided the gases are present in their combining ratios,

the rate of combustion is always directly proportional to the pressure.

2. When the gases are not present in their combining proportions, the rate of combustion is usually proportional to the partial pressure of the combustible gas, which thus becomes the controlling factor. In exceptional cases the rate of combination is strictly proportional to neither of the two gases, but controlled more by the partial pressure of the oxygen than by that of the combustible gas.

3. The catalyzing power of a surface can always be stimulated by previous long exposure at the experimental temperature to the combustible gas. Again, in exceptional cases, similar effects have been observed after exposure to oxygen; but, generally speaking, previous exposure to oxygen reduces, if anything, the activity of a surface.

The principal conclusions established by the experiments are: (*a*) That the power of accelerating gaseous combustion is possessed by *all* surfaces at temperatures below the ignition point, in degrees dependent upon their chemical characters and physical texture: (*b*) that accelerated surface combustion is dependent upon an absorption of the combustible gas (and probably also of the oxygen), whereby it (by the surface) becomes "activated" (probably ionized) by association with the surface: (*c*) that the surface becomes electrically charged during the absorption of the gases (*negative* for the combustible gas and *positive* for oxygen), the charging being due to ionized gas leaving the surface: (*d*) certain important differences from a chemical point of view between homogeneous combustion in ordinary flames and heterogeneous combustion in contact with hot solids have been established, so that there can be no longer any doubt as to the reality of the phenomenon.

Flameless Incandescent Surface Combustion.—My next contention is that if hot surfaces possess the power of accelerating gaseous combustion at temperatures below, or near the ignition point, the same power must be manifested in greater degree at higher temperatures, and especially when the surface itself is incandescent. Indeed, there are experimental grounds for believing that not only does the accelerating influence of the surface rapidly increase with the temperature, but also that the differences between the catalyzing powers of various surfaces, which at low temperatures are often considerable, diminish with ascending temperatures until at bright incandescence they practically disappear.

The considerations I have explained convinced me some years ago that if an explosive gaseous mixture be injected onto or forced through a porous refractory incandescent solid under certain conditions, which will be hereafter explained, a greatly accelerated combustion would take place within the interstices or pores, or, in other words, within the boundary layers between the gaseous and solid phases wherever these may be in contact, and the heat developed by this in-

tensified combustion would maintain the surface in a state of incandescence without any development of flame, thus realizing the conception of flameless incandescent surface combustion as a means of greatly increasing the general efficiency of heating operations.

Some critics while admitting the accelerating influence of an incandescent surface are skeptical about the process being really flameless. The force of such objections largely disappears when we get into close quarters with the phenomenon and realize how extremely slow a transaction flame combustion really is considered in terms of molecular time. Take, for example, the case of such a quick burning mixture as electrolytic gas ($2\text{H}_2 + \text{O}_2$). When this is ignited at atmospheric pressure, the flame is initially propagated by conduction with a uniform slow velocity of 20 meters per second, and during this initial period of "inflammation," which corresponds to the conditions of ordinary flame combustion, the total duration of chemical change in each successive layer is something like $1/50$ second, an interval of at least one hundred million times as long as the average interval between successive molecular collisions in the gas. Even after "detonation" has been set up in the mixture, when the combustion is propagated from layer to layer as a wave of adiabatic compression, at a velocity of 2,820 meters per second, the total duration of chemical change is still of the order of $1/5,000$ to $1/10,000$ second, or about a million times as long as the interval between successive molecular collisions.

The setting up of "detonation" is one, but not the only, way in which ordinary flame combustion can be accelerated and intensified; another way is by bringing into operation the powerful "catalytic" action of an incandescent surface, in the manner which I have already indicated, whereby the whole chemical action is concentrated at the surface, and instantly completed there, *without development of flame*.

To illustrate how a flame may be extinguished by the introduction of an active catalyzing surface, I will perform an experiment first exhibited by my colleague, Professor Strutt. Most of you will be familiar with his discovery of the active modification of nitrogen produced by a powerful electric discharge. This bulb (capacity 300 c. c.) is full of rarefied nitrogen, at a pressure of about $1/10$ mm.; and in the side tube lies an oxidized copper wire, which fits it as closely as is consistent with easy sliding. If now the nitrogen in the bulb be subjected to a powerful electrodeless discharge, it is transformed into an active condition; the gas, as you see, continues to glow brilliantly, owing to the fact that the "active" modification is reverting to the ordinary kind producing a luminosity which may be regarded as a condition analogous with flame. The glow will last for a minute or more during the progress of the chemical reversion, and finally dies out when the latter is completed. But if, on repeating the experiment, the bulb be turned so that the oxidized copper wire drops into the glowing

gas, the luminosity is instantly extinguished. This shows that the reversion process is so enormously accelerated by the surface that practically the whole of the chemical action is concentrated there and instantaneously completed thus extinguishing the glow. I think we have here a close analogy to what I conceive as occurring when an incandescent surface is employed to accelerate ordinary gaseous combustion; the action is so concentrated at the surface that a substantially flameless effect results.

There are two further points which I particularly wish to make clear. In dealing with gaseous interactions at high temperatures, it is necessary to think in terms of what I may call molecular dimensions. Our ordinary units of time, space and mass are altogether too gross, and must be discarded if we wish a true mental picture of the mechanism of combustion. When I speak of combustion as occurring "within the interstices or pores" of an incandescent solid, it must be understood that I mean porosity in a molecular sense. A solid may appear dense, and yet be highly permeable to the molecules of gas; from this point of view only vitreous surfaces, such as glass, are, relatively speaking, nonporous to gases, and even glass when it becomes devitrified is sufficiently porous to induce a slow surface combustion.

Next I want to emphasize that the incandescent solid plays a specific role in surface combustion; it is no mere idle looker-on at the surging crowd of reacting molecules. On the contrary, it so galvanizes and incites the dormant affinities between the combustible gas and oxygen that ordinary combustion gives place to the wild intoxication.

The manner in which the surface acts is still a matter of conjecture, but the fact that it so acts can no longer be disputed. In a discussion at the British Association in 1910, Sir J. J. Thomson insisted that combustion is concerned not only with atoms and molecules, but also with electrons, *i. e.*, bodies of much smaller dimensions and moving with very high velocities, and suggested that in reference to the influence of hot surfaces in promoting combustion it was not improbable that the emission of charged particles from the surface was a factor of primary importance. It is known that incandescent surfaces emit enormous streams of electrons traveling with high velocities, and the actions of these surfaces in promoting combustion may be found to depend on the fact that they bring about the formation of layers of electrified gas in which chemical changes proceed with extraordinarily high velocity.

I have endeavored in this lecture to trace the historic development of the idea that hot surfaces have an accelerating action upon combustion, and to explain my own conception of *flameless incandescent surface combustion*, which phrase, together with the shorter term *surface combustion*, I was the first to apply to a definite condition which my researches had proved to

be a distinct phenomenon, distinguishable from homogeneous flame combustion.

It so happens, however, that subsequent to my visit to America in October, 1911, when I demonstrated and expounded my discoveries before the American Gas Institute at St. Louis, the Chemists' Club, New York, and the Franklin Institute, Philadelphia, Professor C. E. Lucke, of Columbia University, New York, on the basis of some experiments which he made about 1903, and without reference to my later discoveries, has endeavored, without due acknowledgment, to apply the principles disclosed therein to certain domestic and small scale heating operations, on lines already substantially laid down by me. And in connection therewith he has used the term "surface combustion" in a sense which I believe to be as scientifically unwarranted and fundamentally unsound as it is different from that in which it was first used by me.

Professor Lucke disclaimed the operation of catalytic action in his 1903 inventions, which, indeed, were based upon quite other conceptions, and aimed at burning explosive mixtures of gas and air non-explosively and continuously by the use of appliances which (as he thought) would ensure the maintenance of a steady "*flame cap or surface of combustion*" in a given zone, where the velocity of flow of the explosive mixture is just equal to the velocity of back firing. Apparently he did little or nothing between 1903 and my visit to America in 1911 to develop his ideas, but since 1911 he has resumed and, profiting by the great interest aroused by my lectures and experimental demonstrations, he is now appearing as a pioneer in "surface combustion."

In the course of the discussion following a lecture which he gave October 14th, 1913, to the American Gas Institute upon "The Design of Surface Combustion Appliances," he delivered himself of the following curious conception in reply to the question: "Why does the name surface combustion apply to this method?" The answer given by Professor Lucke was:

"Gas burning alone would give a big volume of flame. The flame itself would fill much space. By using pre-mixed air with the gas the flame volume is reduced. The total cubic feet occupied is less and less, until just at the combining proportions the flame volume becomes zero and is replaced by a surface instead" . . . (there) . . . "will be length and breadth of flame without any thickness, so it is surface combustion."

In answer to a further question as to where the temperature would be developed, he replied, "Right where the flame is." And on being further asked, "On the surface?" he replied, "Where the flow velocity is equal to the rate of propagation."

A scientific investigator must expect to find other workers anxious to adopt and apply the results of his discoveries, and I do not complain of Professor Lucke helping forward in America the development of principles which I first demonstrated there in 1911, al-

though I think he ought to have made due acknowledgment of that fact. But I must protest against his recent attempt to confuse his previous notion of a "flame cap or surface of combustion" (which I believe to be erroneous) with my later conception of "surface combustion," inasmuch as the two are not only clearly distinct, but mutually incompatible.

It was in 1906, after the publication of the first installment of my scientific researches in conjunction with Mr. R. V. Wheeler, that I decided to develop my ideas technically at the first favorable opportunity, and in December of that year I made a provisional arrangement with Messrs. Wilsons and Mathiesons, Ltd., to co-operate with them on the matter. Before, however, we had proceeded very far, an unlooked-for intervention occurred in 1907.

When I resumed my interrupted co-operation with Messrs. Wilsons and Mathiesons, October, 1909, Mr. C. D. McCourt became associated with the enterprise; and, with his assistance, steps were at once taken to attack the problem systematically from the industrial standpoint.

Before any further experiments were made, I deposited with a bank on October 16, 1909, a signed statement in a sealed envelope, which was not opened until October 23rd, 1913, defining the nature of the problem, and my proposed solution of it, in the following terms:

"To bring a combustible mixture of gas and air in suitable proportions into contact with the interstices of an incandescent porous solid or suitable composition and porosity in such a manner as to produce a flameless, or as nearly as may be a flameless surface or interstitial combustion, whereby the porous solid shall be maintained in a continual state of incandescence."

How closely the realization of the phenomenon, in the two processes which I propose to describe and illustrate, has corresponded to this original definition of it, I leave you to judge; but I wish to place this definition on record, as evidence of the precise position to which the scientific researches in the laboratory had led us before industrial investigation had begun.

The new system of incandescent surface combustion, known as the "Bonecourt" system, which was evolved under my direction during the three following years, consisted principally of two processes, in which a homogeneous explosive mixture of gas and air, in the proper proportions for complete combustion (or with air in slight excess), is caused to burn without flame in contact with a granular incandescent solid, whereby a large proportion of the potential energy of the gas is immediately converted into radiant form.

The advantages claimed for the new system are: (1) The combustion is greatly accelerated by the incandescent surface, and, if so desired, may be concentrated just where the heat is required; (2) the combustion is perfect with a minimum excess of air; (3)

the attainment of very high temperatures is possible without the aid of elaborate heat recuperative and regenerative devices; and (4) owing to the large amount of radiant energy developed, transmission of heat from the seat of combustion to the object to be heated is very rapid. These advantages are so uniquely combined in the new system that the resultant heating effect is for many important purposes not only pre-eminently economical but also easy of control.

Diaphragm Heating and Its Applications.—In the first process the homogeneous mixture of gas and air is allowed to flow under slight pressure through a porous diaphragm of refractory material from a suitable feeding chamber (see Fig. 2) and is caused to burn without flame at the surface of exit, which is thereby maintained in a state of incandescence. The diaphragm is composed of granules of firebrick, or

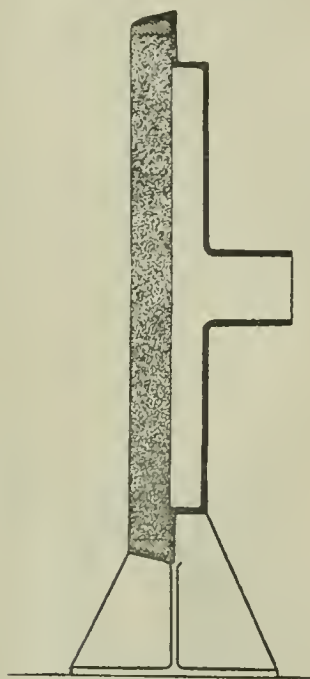


Fig. 2.

other material, bound together into a coherent block; the porosity of the diaphragm graded to suit the particular gas for which it is to be used. The diaphragm is mounted in a suitable casing, the space enclosed between the back of the casing and the diaphragm constituting a convenient feeding-chamber for the gaseous mixture which is introduced at the back. Such a mixture may be obtained in either of two ways, namely, (1) by means of suitable connections through a Y-piece with separate supplies of low-pressure gas and air (2 or 3 ins. W. G. is sufficient), or (2) by means of an "injector" arrangement connected with a supply of gas at a pressure of 1 to 2 lbs. per square inch; the gas in this case draws in its own air from the atmosphere in sufficient quantity for complete combustion, the proportions of gas and air being easily regulated.

We will now start up a diaphragm. Gas is first turned on and ignited as it issues at the surface; air is then gradually added until a fully aerated mixture

is obtained. The flame soon becomes non-luminous, and diminishes in size; a moment later it retreats to the surface of the diaphragm, which at once assumes a bluish appearance; soon, however, the granules at the surface attain an incipient red heat, producing a curious mottled effect; finally, the whole of the surface layer of granules becomes red hot, and an accelerated "surface combustion" comes into play. All signs of flame disappear, and there remains an intensely glowing surface throwing out a genial, radiant heat.

Whilst the diaphragm is in operation I may point out some of the more striking features of the phenomenon. I. The actual combustion is confined within a very thin layer— $\frac{1}{8}$ to $\frac{1}{4}$ inch immediately below the surface, and no heat is developed in any other part of the apparatus; the back of the apparatus is so cold that I can lay my hand on it. II. The combustion of the gas, although confined within such narrow limits, is perfect, for when once the proportions of gas and air is properly adjusted, no unburnt gas escapes from the surface. III. The temperature at the surface of the diaphragm can be instantly varied by altering the rate of feeding of the gaseous mixture; there is practically no lag in the temperate response, a circumstance of great importance in operations where a fine regulation of heat is required. IV. A plane diaphragm such as this may be used in any position, *i. e.*, at any desired angle between horizontal and vertical. V. The diaphragm method is amenable to a variety of combustible gases; coal or coke-oven gas, natural gas, petrol-air gas, carburetted water gas, are all well suited in cases where unimpeded radiation is required. Finally, the incandescence in no way depends upon the external atmosphere. When once the diaphragm has become incandescent, and the proportions of air and gas properly adjusted, the surface will maintain its incandescence even in an atmosphere of carbon dioxide.

I do not point out to you the many obvious purposes, domestic and industrial, to which "diaphragm heating" may be applied. In the domestic line the boiling of water, grilling, roasting, and toasting, are at once suggested; and, although the best existing types of gas fires are thoroughly hygienic and efficient, I think that the diaphragm may come in for the heating of apartments.

I have been told of a restaurant in London where they are grilling by means of an electric radiator fixed above the work so that the radiant energy is directed downwards onto it. It is claimed that the value of the recovered fat, which in the ordinary method drops into the fire and is consumed, has more than paid for the electricity used. With a diaphragm, similar advantages can be secured with gas at a considerable less cost; for comparing gas of 500 B. T. U. per cu. ft. at 2s 6d per 1,000 cu. ft. with electricity at 3d per unit, the cost of a given amount of energy is about fourteen times greater in the form of electricity than in the form of gas.

Not long ago I visited a candy factory where dia-

phragms have been employed for more than a year for the boiling and concentrating of sugar solutions. The solution is boiled in a copper pan over a 13-in. diameter circular diaphragm (Fig. 3); the supply of gaseous mixture is controlled by one lever which operates the gas and air cocks. Ignition is effected by a pilot light. Each boiler does 10 to 12 heats per diem, each lasting 20 minutes, and some of the diaphragms have been in continuous daily use for a year. They have 13 such boiling pans in constant use, and the gas consumption is not more than half what it was when the pans were heated over ordinary atmospheric flame burners. The secret of this higher efficiency lies in the fact that gas flames are a very unsatisfactory means for boiling liquids in metallic vessels, owing to the non-conducting layer of relatively cool gas which forms between the flame and the undersurface of the pan, but with a diaphragm the large percentage of ra-

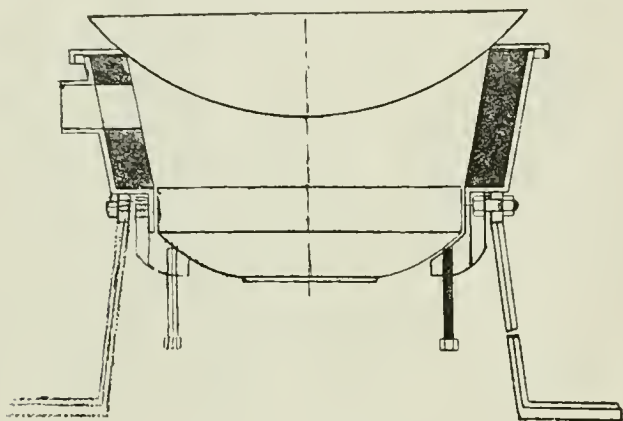


Fig. 3. Diaphragm for Boiling Sugar Solutions.

diant heat is quickly absorbed by the vessel and is transferred to the liquid with high efficiency.

Another interesting application of diaphragm heating is for the evaporation and concentration of liquids by means of downward radiation from a diaphragm above the surface of the liquid. By this process, only the topmost layers of the liquid are heated; the radiant energy from the incandescent diaphragm is transmitted to the surface of the liquid, where it is absorbed and utilized for evaporation. The material separates out as a surface skin; it is then dried by the radiant heat, and at intervals the dry crust may be skimmed off. The advantages of such a method for the evaporation of liquids are obvious, but, of course, its commercial development is primarily a question not so much of actual thermal economy as of the cost of gaseous fuel compared with coal. Thus, with coal at 12s per ton and coal gas at 1s per 1,000 cu. ft., the cost of a given number of heat units is about four and a half times as great in the form of gas than in coal, although the greater economies and other advantages obtainable with gas largely wipe out the difference in final cost. In localities near coking plants, coke oven gas should be obtainable at a price which

would make this particular use of the diaphragm a commercial proposition.

Surface Combustion in a Bed of Refractory Granular Material.—This process is applicable to all kinds of gaseous or vaporized fuels, and consists essentially in injecting, through a suitable orifice at a speed greater than the velocity of back-firing, an explosive mixture into a bed of incandescent granular refractory material, which is disposed around or in proximity to the body to be heated.

Fig. 4 shows the process as applied to a crucible furnace, the crucible surrounded by a bed of refractory incandescent granular material. The mixture of gas and air is injected at a high velocity through an orifice at the base of the furnace, and as it impinges upon the incandescent bed combustion is instantaneously completed without flame. The seat of this active surface combustion is in the lowest part of the bed; the burnt gases, rising through the upper layers, rapidly impart their heat to the bed, maintaining it in a high degree of incandescence.

It is obvious that this process is capable of adaptation to all kinds of furnace operations, the heating of crucibles, muffles, retorts, and to annealing and forging furnaces generally. Moreover, it is not essential that the bed or refractory material be very deep; quite

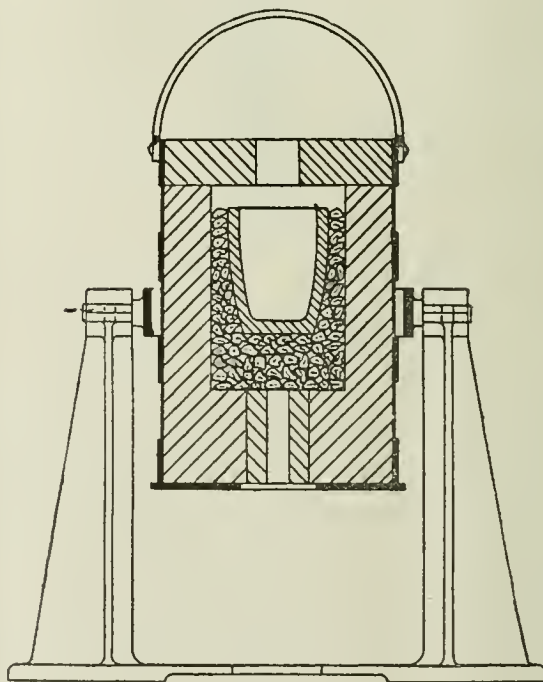


Fig. 4.

a shallow bed suffices to complete the combustion. Neither is it necessary the bed be disposed *around* the vessel or chamber to be heated; for if contact with the burnt products is not objectionable, a shallow bed may be arranged *within* the heating-chamber itself; or the refractory material may be equally well packed into tubes or the like, traversing the substance or medium to be heated. The last-named modification is

specially important in relation to steam-raising in multi-tubular boilers.

To demonstrate the application of this process to furnace operations we will start up the small muffle furnace. We first turn on the gas and light it as it issues from the hole in the cover of the furnace; the air supply is then gradually opened until the flame strikes back through the granular material in which the muffle is imbedded until it is arrested at the orifice in the base of the furnace through which the explosive mixture enters. The flame quickly raises the granules in the neighborhood of this orifice to a state of incandescence, when "surface combustion" supersedes the flame. As soon as the lower regions of the granular bed have become thoroughly incandescent, the rate at which the mixture is being fed may be materially increased, so that in a few minutes the whole of the bed is incandescent.

By means of this process much higher temperatures are attainable with a given gas than by the ordinary methods of flame combustion without a regenerative system, and, as a matter of fact, we have found that with any gas of high calorific intensity the upper practical temperature limit is determined by the refractoriness of the material composing the chamber to be heated (*i. e.*, the muffle or crucible) rather than by the possibilities of the combustion. When I tell you that in a crucible fired by coal gas on this system we have melted Seger-cone No. 39, which melts at 1880° C. (3416° F.), and also that we can easily melt platinum, you will appreciate the possibilities of the method.

The maximum temperature obtainable, without "regenerative" appliances, with any particular gas will obviously depend upon the relative heat capacities of their products of combustion for a given heat development in the bed. In this connection it is of interest to compare the principal gaseous fuels available for industrial operations in the order of their calorific intensities.

COMBUSTION OF TYPICAL GASEOUS FUELS.

	Per Cubic Foot of Gas Burned,	Per 100 B. T. U.'s net Developed on Combustion.					
		Net B. T. U.	Vol. of Air Required.	Vol. of Products.	Vol. of Air Required.	Vol. of Combining Mixtures.	Vol. of Products.
Blue water gas	290	2,290	2.82	0.79	1.14	0.97	0.95
Coal or coke oven gas	500	4,656	5.36	0.93	1.13	1.08	1.00
Producer gas	140	1,166	2.00	0.84	1.50	1.13	1.38
Blast furnace gas	100	0.716	1.58	0.72	1.72	1.58	1.52

Now, whilst with coal gas, coke-oven gas, or water gas, it should be easily possible, without regeneration, to obtain in a refracting granular bed temperatures of up to at least 2000° C. (or say 3630° F.), with a low-grade producer gas, such as Mond gas, about 1500° C. would probably be the approximate maximum without regeneration. With some degree of

heat recuperation, which in large furnaces is quite practicable, still higher temperatures would be attainable.

The heating also within the maximum limits, with any kind of gas, is very uniform, economical, and easily controlled. Indeed the temperature for a given furnace fired by a gas of given uniform quality is chiefly determined by the amount of gas burnt per unit time in the bed, or, in other words, by the rate of heat developments in the bed.

In order to give you some idea of the thermal efficiency as compared with the ordinary methods of flame heating, I give below results of a test on a surface combustion furnace in which a muffle 9¼ ins. long by 5½ ins. wide by 3¼ ins. high was maintained at temperatures between 815° and 1425° C. with coal gas of 540° B. T. U. (net).

Observe that the temperature of the products is 300° to 350° C. lower than that of the muffle, and that even with a muffle temperature of 1424° C. there was no appearance of flame at the top of the furnace. The gas consumptions recorded are extremely economical in comparison with those required for ordinary heating by daily contact. In a similar test with a muffle of the same size heated by flame contact, the gas consumption to maintain the muffle at 1055° C. (the maximum temperature obtainable) was 105 cu. ft. per hour, whereas consumption on the surface combustion furnace at the same temperature would have been about 43 cu. ft. per hour. The results of these and other similar tests carried out 3 years ago in Leeds upon medium-sized muffle furnaces proved that to maintain a given temperature between 800° and 1400° C. a properly constructed surface combustion furnace required from 70 to 40 per cent only of the gas used in an ordinary flame heated furnace of the same dimensions. The advantage in favor of surface combustion increases with the working temperature.

Temp. in Middle of Muffle		Gas Consumption to Maintain Temp. Constant		Temp. of Products	
Degs. C.	Degs. F.	Cubic Feet per Hour at 15° C.		Degs. C.	Degs. F.
815	1,499	21.0		540	1,004
1,004	1,840	35.3		645	1,193
1,205	2,201	58.0		870	1,598
1,424	2,595	79.0		1,085	1,985

This conclusion was confirmed by independent trials in New York shortly after my lecture there in 1911, in which a surface combustion muffle furnace was pitted against the best American types of similar dimensions, with the result that to maintain a temperature of 1400° C. we practically halved our gas consumption, whilst to maintain 800° C. our consumption was about 0.7 of theirs.

In large muffle furnaces regenerative arrangements may advantageously be added. By way of example, I show a regenerative furnace (Fig. 5) for the heating of a muffle chamber 8 ft. by 3 ft. by 3 ft., which was successfully fired by coal gas at our experimental station, in 1912, the air supply being pre-heated to

300° C. by the sensible heat of the waste gases leaving the combustion bed. The mixture of coal gas and pre-heated air was fed in at the front end of the furnace, and burned flamelessly in contact with a bed of incandescent granular material surrounding the muffle chamber *A*; the hot products of combustion leaving the bed were then led downwards through a second granular bed disposed round a system of iron pipes through which the air supply was fed. By means of this device we were able to maintain the muffle at 1000° C. while the waste gases left the system at less than 200° C.

There is another type of furnace for high temperature operation, in which the heating is effected by means of two parallel granular beds along each side of the working space, which is therefore filled with the burnt gases. The latter are then led away through a flue vent at the back, downwards under the floor of

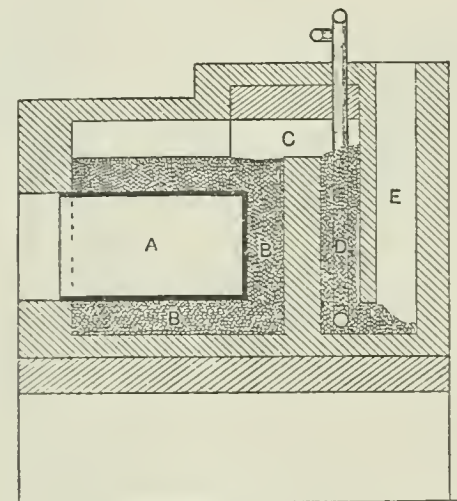


Fig. 5.

the working space, and thence are discharged into the atmosphere.

This type of furnace can also be combined with a simple heat recuperative system, and as an example of what can be done with such a combination, I give the results of a trial run, Table I, with a furnace (working space 3 ft. 1 in. by 3 ft. 2 in. by 1 ft. 6 in.), fired by washed producer gas (generated from anthracite) of average *net* calorific value 139 B. T. U., both gas and air being regenerated.

TABLE I.

Hour.	Rate of gas consumption, Cubic feet per hour.	Furnace temperature, degs. C.	—Temperature of—		
			Hot gas, Degs. C.	Hot air, Degs. C.	Burnt products, Degs. C.
9:35 a. m.	7,360	800	105	148	172
10:0	7,280	985	129	191	206
11:0	6,720	1,220	184	264	283
12:0 noon	6,280	1,305	261	309	328
1:30 p. m.	4,920	1,365	295	...	...
3:45	5,200	1,410	320	...	400
5:0	4,920	1,395	...	...	390

The furnace having been started up, systematic observation of (*a*) rate of gas consumption, (*b*) furnace temperature, and (*c*) temperatures of the hot air and hot gas leaving the generator tubes, as well as of the burnt product finally leaving the system, were made at intervals throughout the day, until a temperature of 1400° C. had been reached and maintained for a couple of hours.

From analyses of (*a*) the producer gas and (*b*) the burnt products leaving the system it will be seen (1) that combustion was practically perfect with only a small excess of air, and (2) that the products finally left the system at a temperature 1000° C. *below* that of the furnace.

ANALYSES OF THE PRODUCER GAS.

	10 a. m.	Noon.	3 p. m.	Mean.
CO ₂	5.8	6.4	4.7	5.60
CO	22.6	23.3	25.0	23.60
H ₂	15.4	15.7	15.4	15.50
CH ₄	1.4	1.4	1.7	1.50
O ₂	1.2	1.0	1.2	1.15
N ₂	53.6	52.2	52.0	52.65

ANALYSES OF BURNT GASES LEAVING FURNACE.

	10 a. m.	Noon.	3 p. m.	Noon.
CO ₂	16.4	16.7	17.0	16.70
CO	0.3	0.2	0.2	0.23
O ₂	2.0	2.4	2.0	2.13
N ₂	81.3	80.7	80.8	81.94

The primary difficulty, met with in all high temperature work, is finding suitable refractory materials to withstand the fierce combustion. Then there are problems connected with feeding and distribution of the gaseous mixture, with the arrangement and dimensions of the combustion beds, and the contour of the furnace, all of which must be solved for each type of industrial requirement. Moreover, would-be designers and users of surface combustion furnaces must acquire an understanding of what surface combustion really is before they can realize fully its possibilities; and people whose experience has been on the old system of flame heating must be prepared to unlearn a good deal and revise their notions. A new and sound principle *wrongly* applied may give no better (if as good) results as a familiar and yet inferior principle *rightly* applied; everything depends upon right application which knowledge and right understanding alone ensure.

Nevertheless, judging from reports that reach me from time to time, substantial progress has been and is being made in the direction of gas-fired, tilting crucible furnaces for brass and aluminum melting, annealing and forging furnaces, which, I am given to understand, are now running satisfactorily in industrial establishments on both Mond gas and town's gas.

I now come to an interesting modification of the "granular bed" process, as applicable to the continuous melting of easily fusible metals such as lead or type metal, in which the granular material is packed into tubes traversing the medium to be heated. The experiments I am about to describe refer to lead melting and were carried out in Leeds under my direction, and the method is, in principle, the same as employed in the "Bonecourt" boiler.

Fig. 6 represents an iron tank, efficiently lagged and filled with molten lead at a temperature some 50° C. above its melting point. In the molten bath is a vertical iron tube, 3 ft. long and 3 ins. in internal diameter, packed with granular refractory material. At the bottom of the tube is a tightly fitting cylindrical plug of refractory material, with a circular $\frac{3}{4}$ -in. passage for the admission of the explosive mixture of gas and air, which is caused to burn flamelessly as it impinges upon the incandescent granular material above the plug; the burnt products pass upwards through the remainder of the packing, imparting their residual heat to the bath, and finally exit through the open end of the tube at about 130° C. only above the

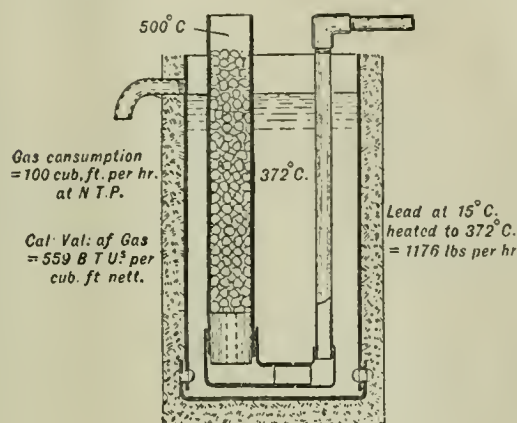


Fig. 6.

temperature of the metal in the bath. Solid lead is fed continuously into the tank, and the molten metal is run over through the spout.

The following are results of a trial run:

LEAD MELTING TEST.

	Degs. C.	Degs. F.
Temperature of metal charged	15	60
Temperature of metal tapped	372	702
Temperature of gases leaving apparatus	500	932
Lead melted per hour=1,176 pounds.		
Gas burnt per hour=100 cubic feet.		
Net calorific value of gas=559 B.T.U.		

Lead ingots, weighing about 30 lbs., were added at intervals of $1\frac{1}{2}$ minutes, and the molten metal displaced was simultaneously run off into moulds. Care was taken to keep the bath thoroughly molten and at a temperature within a few degrees of the mean value. Burning gas net calorific value 559 B. T. U., 100 cu. ft. per hour, it was possible to raise the temperature of 1,176 lbs. of lead per hour from 15° to 372° C., the temperature of the products of combustion leaving the tube keeping constant at 500° C., or only 128° above the temperature of the molten metal. From the latest determination of the specific heat of lead at temperatures up to and above its melting point, and adopting the usually accepted value for the latent heat of fusion, I calculate that the heat required to raise the temperature of 1 lb. of lead from 15° C. to 372° C. (including melting) is 32/67 B. T. U. There-

fore the heat transmitted to the lead per hour was 38,420 B. T. U.; and the net calorific value of the gas was 55,900, the ratio $\frac{38,420}{55,900} = 0.686$. However, as

the net heat of combustion of the gas is based on the assumption that the products of combustion (less steam) are cooled down to 15° C., whereas in the experiment the temperature of the molten metal was 372° C., it follows that the high ratio of 0.686 does not do full justice to the merits of the system. Under "ideal" conditions, the temperature of the gases leaving the combustion tube could not have been reduced to below 372° C.; it was actually reduced to within 130° of this "ideal" limit. Taking these circumstances into consideration, I calculate that the efficiency of the melting operation was practically 80 per cent of that theoretically possible.

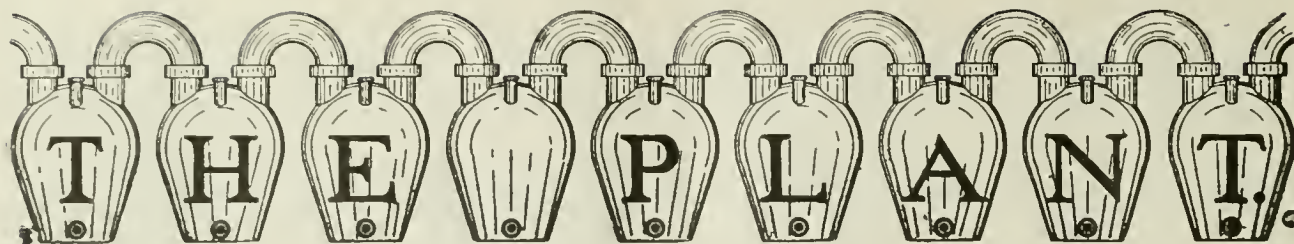
WAR AFFECTS COPPER PRODUCTION.

With the possible exception of the silver industry, the copper industry will probably feel the injurious effects of the European war more seriously than any other of the leading American metal industries. During the last five years approximately 50 per cent of the copper turned out by American refineries has been exported, in large part, to the countries now involved in the European war, according to the United States Geological Survey. Some of this copper has been imported for metallurgical treatment, and the imports will probably be somewhat restricted on account of shipping conditions.

During these five years, however, domestic consumers have taken only about 63 to 67 per cent of the copper produced from mines within the United States, so it is evident that there must be a material curtailment of production while present conditions prevail. Considerable copper is of course consumed in munitions of war and for other military purposes, but the constructive arts of peace are far more favorable for the copper industry than the destructive art of war.

American producers have already greatly curtailed their production, and it seems almost certain that the output must be materially restricted for an indefinite period, dependent largely on the European conditions.

The amount of sulphur produced in the United States in 1913, according to the U. S. Geological Survey, was 311,590 long tons, valued at \$5,479,849, the greatest output in the history of the industry. This output was 8,118 long tons greater than that of 1912 and showed an increase in value of \$223,427. In 1913 three states produced sulphur, namely, Louisiana, Texas, and Wyoming. The United States is rapidly gaining on Sicily, which at the present time is the leading sulphur-producing country in the world and whose output for the year ending July 31, 1913, was 346,213 long tons.



DISTILLATION OF RESINOUS WOOD BY SATURATED STEAM.*

By L. F. HAWLEY and R. C. PALMER.

COMMERCIAL STEAM DISTILLATION PROCESSES.

The steam distillation process for obtaining the volatile oils from the wood of the longleaf pine has been the basis of a small industry since about 1903, being introduced apparently in an attempt to produce wood turpentine at temperatures lower than those used in the destructive distillation processes then in operation, and thus to obtain a product uncontaminated by the decomposition products of wood and rosin. Quite a large number of plants have been built to use either sawmill waste or lightwood, or both, but many have been abandoned, probably only 12 or 15 being in operation in 1911. The quality of the crude turpentine produced has usually been very good, but because this is the only product obtained, or because the yield of this product is often lower than that of "crude turpentine" from other processes, the plants have been successful only under especially favorable conditions.

This process seems to be very promising, however, when combined with other processes for the utilization of the steamed chips, as for instance the extraction of the chips with volatile solvents for the removal of the rosin. Conditions are also favorable for this process in cases where the material would be largely used as fuel or wasted, or is very cheap or so poor in quality that more complicated processes would not be profitable; these conditions are commonly realized in the case of that part of the waste wood of sawmills now used as fuel at the plant or burned on the rubbish pile.

PURPOSE OF INVESTIGATION.

In the fields mentioned above the steam distillation of resinous woods will undoubtedly expand and it was in the hope of promoting this expansion and thus increasing the utilization of a class of material now wasted that this investigation on the fundamentals of the process was undertaken. There has been no uniformity in commercial practice or in the opinions of the various operators and no experimental data have been published on the effects produced by the different readily controlled variables, such as steam pressure, size of chips, or rapidity of distillation. In the methods described in various patent specifications the greatest stress has been laid on the mechanical features of charging and discharging, and of distributing the

steam throughout the retort, which, although of great importance in the economy of a commercial method, throw no light on other equally important factors.

There seemed to be, therefore, a profitable field for investigation in determining the relations between the conditions under which the distillation is conducted, on one hand, and on the other hand the amount and kind of products and the readiness with which they are obtained.

THEORETICAL CONSIDERATIONS.

In the description of the experimental work and the discussion of the results it will be necessary to refer constantly to certain theoretical principles which apply to the distillation of volatile oils with steam, and in order to make the future discussions clearer, a brief presentation of these principles is given at this time.

In order to simplify the deductions, the following assumptions are made in regard to the resinous material contained in the "lightwood" from the longleaf pine:¹

1. It is composed only of turpentine, pine oil,² and rosin.
2. The components are all simple substances completely soluble in one another.
3. None of the components are soluble in water.
4. The turpentine and pine oil are both volatile, but the turpentine has the lower boiling point.
5. Rosin is nonvolatile.

While these assumptions are not strictly true in all cases, none of them are sufficiently incorrect to affect seriously the conclusions.

Concerning the distillation with steam of the resinous material defined by the above assumptions, the following deductions can be made:

1. There will be a separation of the two volatile constituents, the turpentine being in greater proportion in the first part of the distillate and the pine oil in the latter part.
2. The temperature of the distillation under normal pressure will be slightly above 95° C. at the begin-

¹M. Vezes (Bull. Soc. Chim., 29, 470-478 (1903)) has given a very clear and complete discussion of the principles underlying the distillation of the oleoresin from the Maritime pine of France. For the simplification of the discussion the following assumptions were made: (1) That the oleoresin is composed only of essence (turpentine) and colophony (rosin). (2) That these components are both simple substances completely soluble in each other. (3) That neither is soluble in water. (4) That rosin is nonvolatile. In regard to the oleoresin obtained by shipping the live long leaf pine tree of the United States, the same assumption can be made, but the oleoresin contained in the pitchy "lightwood" from this species has another component, the heavy, high-boiling "pine oil" which must be taken into consideration in the discussion of the steam distillation of such wood.

²A discussion of the occurrence of pine oil in the "lightwood" of longleaf pine is given in Forest Service Bulletin 105 ("Wood Turpentine, Their Analysis, Refining and Composition." by L. F. Hawley).

*Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

ning, and will rise throughout the distillation, never, quite reaching 100°C. , however, as long as any of the turpentine or pine oil remains undistilled.

3. If the pressure at which the distillation is carried on is increased the temperature will be increased, the temperature depending upon the pressure and on the concentrations of the turpentine, pine oil, and rosin; the temperature will, however, never reach the steam temperature corresponding to the pressures used as long as any turpentine or pine oil remains undistilled.

4. The proportion of water to oil in the distillate will increase as the distillation progresses, this proportion being influenced only by the relative amounts

to the manner in which they affect the completeness of the equilibrium in the system, or in other words, the completeness of contact between the oleoresin and the steam. In the same way the effects (other than temperature changes) of steam pressure on the results of the distillation are also due to its influence on the completeness of contact between steam and oleoresin rather than to any influence on the behavior of the steam and oleoresin when completely in equilibrium.

EXPERIMENTAL METHODS.

APPARATUS AND MATERIALS.

The general procedure was to distil charges of the same sized chips under different conditions, and of different sized chips under identical conditions, and to note carefully the variations in the results of the distillations. It was not practicable to make all the runs on exactly comparable material, because a large number of charges of equal resin content could not be secured, and because the material could not be kept without some loss of volatile oil by evaporation. The runs were therefore made in groups with comparable material in each group; the results from each group were made comparable to some extent with those from other groups by a comparison of the resin content of the different groups. This was readily accomplished by distilling the sawdust obtained in the preparation of the material for each group, as this sawdust was a good average sample of the whole group.

A sketch of the retort used for the distillations is shown in Fig. 1. This retort was designed for use in extraction of tannin from wood and bark, as well as for distillation experiments; it was therefore made of copper and had the closed steam coils *B*. The perforated plate *C* was designed to hold up the charge while the lower head of the retort was taken off; then by revolving the plate until the slots *E* came opposite the supporting lugs *F*, the plate falls and the charge can be removed. The pressure gage was attached at *D*. The other parts of the retort require no special description. An ordinary copper worm condenser was used and the distillate was caught in 1-liter graduated cylinders.

The J. G. Newman Lumber Co., of Hattiesburg, Miss., furnished for the experiments a large log of pitchy lightwood in which the pitch was distributed with unusual evenness. From this log it was possible to prepare a number of charges of chips, of which all from one portion of the log were similar in resin content.

PREPARATION OF MATERIAL

The method of selecting material so that each charge should be comparable with the other charges in the same group is shown in Table I and Fig. 2. The sticks were sawed into sections at one time, but usually the sections were chipped only as required; that is, just before each distillation. Thus the sections for the last runs of a group had been longer cut than those of the

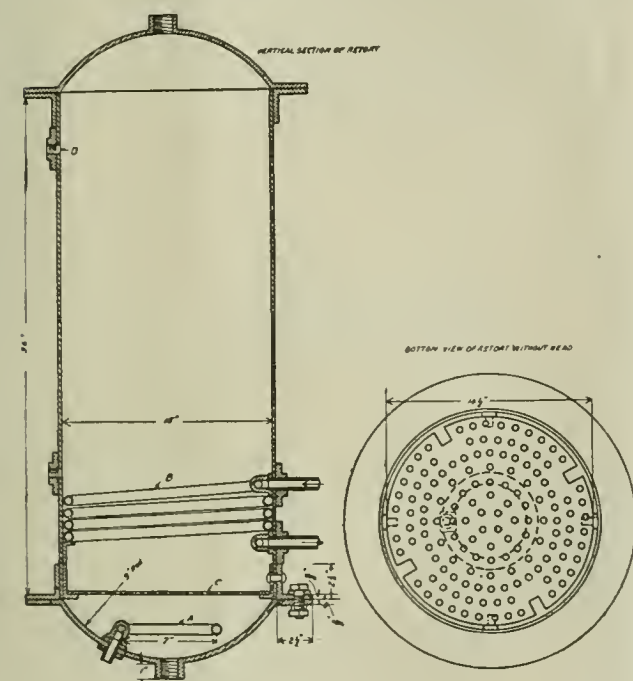


Fig. 1. Sketch of Retort.

of the different constituents present in the oleoresin being distilled.³

In these deductions it is considered that the system is in complete equilibrium and under such conditions the behavior of this oleoresin when distilled with steam could be foretold with considerable accuracy, but in the distillation of wood containing the oleoresin, there is a disturbing factor introduced which makes necessary the investigation of the variable mentioned in the introduction. This disturbing factor is the difficulty of keeping a complete equilibrium between the oleoresin and the steam, due to the fact that the wood surrounds the oleoresin and tends to keep the steam from coming in contact with it.

The effects of the size of chips and the rapidity of distillation are not due to a change of the laws governing the distillation of the oleoresin with steam, but

³A change in the pressure at which the distillation is carried on might change the proportion of water to oil in the distillate, but this change would be only slight and there is not sufficient data available to decide even the direction of this change.

first runs, and although they were kept in covered cans, or if without cover were piled close together, there was still some chance of loss by volatilization, especially when some time intervened, as in the large number of runs in Group I. To lessen the loss by volatilization during the chipping process, the chips were covered with water as fast as they were made. The sawdust charges were put into the retort without any delay after collection, except in runs 2 and 3, which were prepared and collected but not distilled at the same time with run 1.

DISTILLATION.

Only a general description of the procedure will be given here; the same general methods were used in all cases and the details are given later in the tabulated record of the runs.

REGULATION.

The speed and pressure of the distillations were reg-

ulated simply by the inlet valve at the bottom and by the outlet valve at the top of the retort. During distillation at atmospheric pressure the outlet valve was left open and the speed regulated by the inlet valve alone; but during distillation at higher pressure it was of course, necessary to use both valves in order to keep both speed and pressure at the required values. The variation in speed was never more than one-half minute per liter of distillate, and in pressure never more than 2 pounds per square inch from the required values.

Data Obtained.—A typical data sheet giving an example of the records obtained in each distillation is shown in Table I. The distillate was caught in one-liter fractions and the time and pressure were recorded with every fraction. The amount of oil in each liter of distillate was determined as accurately as possible while in the original receiver (one-liter cylinders grad-

TABLE I.—EXPERIMENTAL RUNS MADE AND MATERIAL USED IN EACH.

Group No.	Run No.	Block.	Material used		Size of chips. Inches.	Remarks.	
			Sticks.	Sections.			
I	1	A			Sawdust	Obtained in cutting sections.	
	2	A			Sawdust	Obtained in cutting sections.	
	3	A			Sawdust	Obtained in cutting sections.	
	4	A	I to VII....	10, 22, 28.....	1x1		
	5	A	I to VII....	6, 18, 29.....	$\frac{1}{4} \times \frac{1}{8}$		
	6	A	I to VII....	4, 17, 30.....	$\frac{1}{2} \times \frac{1}{4}$		
	7	A	I to VII....	2, 14, 25.....	$\frac{1}{4} \times \frac{1}{8}$		
	8	A	} I to VII..	{ 3, 5, 9, 11.....	$\frac{1}{4} \times \frac{1}{8}$	{ Chips from each section divided among the three runs.	
	9	A		{ 13, 15, 19, 21.....			
	10	A		{ 23, 26, 27, 31....			
II	11	A			Sawdust	Obtained in sawing slabs.	
	12	A			1 x variable	{ Sections of slabs.	
	13	..			6 x same Inches.		
III	14	A	I to VII....	{ 1, 7, 8, 12, 16....	$\frac{1}{32}$ of section	{ One-half of each section used in each run.	
	15	A	I to VII....	{ 20, 24, 32, 33....	$\frac{1}{2}$ of section		
IV	16	B			Sawdust	Obtained in cutting sections.	
	17	B	I to VII....	} All odd numbers.	$\frac{1}{4} \times \frac{1}{8}$	Chips from each section divided between each run.	
	18	B	I to VII....				
	19	B	I to VII....	} All even numbers	$\frac{1}{2} \times \frac{1}{2}$	Chips from each section divided between each run.	
	20	B	I to VII....				
V	21	C			Sawdust	Obtained in cutting sections.	
	22	B	{ I, IV, VII..	1, 4, 7, 10.....	} 2x2		
			{ III, VI.....	2, 5, 8, 11.....			
			{ II, V.....	3, 6, 9, 12.....			
	23	C	{ III, VI.....	1, 4, 7, 10.....	} 2x2		
			{ II, V.....	2, 5, 8, 11.....			
			{ I, IV, VII..	3, 6, 9, 12.....			
	24	..	{ II, V.....	1, 4, 7, 10.....	} 4x4		
			{ I, IV, VII..	2, 5, 8, 11.....			
			{ III, VI.....	3, 6, 9, 12.....			
VI	25	D			Sawdust		Obtained in cutting sections and in slabbing blocks. Obtained in cutting sections.
	26	D	I to VIII....	1, 4, 6, 9.....	1x1		
	27	D	I to VIII....	2, 5, 8.....	1x1		
	28	D	I to VIII....	3, 7.....	1x1		
VII	29	E			Sawdust		
	30	E	{ I, V.....	1, 5, 9, 13.....	} Shavings		
			{ II, VI.....	4, 8, 12, 16.....			
			{ III, VII....	3, 7, 11, 15.....			
			{ IV.....	2, 6, 10, 14.....			
	31	E	{ I, V.....	3, 7, 11, 15.....	} Shavings		
			{ II, VI.....	2, 6, 10, 14.....			
			{ III, VII....	1, 5, 9, 13.....			
			{ IV.....	4, 8, 12, 16.....			
	32	E	{ II, VI.....	2, 6, 10, 14.....	$\frac{1}{2} \times \frac{1}{2}$		
			{ II, V.....	1, 5, 9, 13.....			
			{ III, VII....	4, 8, 12, 16.....			
			{ IV.....	3, 7, 11, 15.....			
	33	E	{ I, V.....	4, 8, 12, 16.....	$\frac{1}{2} \times \frac{1}{2}$		
			{ II, VI.....	3, 7, 11, 15.....			
			{ II, VII....	2, 6, 10, 14.....			
			{ IV.....	1, 5, 9, 13.....			

uated to 10 cc.); the oil was then separated from the water in a separatory funnel and its specific gravity determined. When the amount of oil in the fractions was so small that a specific gravity determination could not readily be made on a single fraction, the oil from a sufficient number of fractions was combined to make the determination possible. As a check on the total amount of oil computed from the rough measurements on the separate fractions, the combined oil from all the fractions or from the fractions of different portions of the distillation was accurately measured.

The detailed records for each distillation will not be given in this report, but instead the essential part of this data will be tabulated together with other factors computed from the data. The discussion of the data from all groups will be taken up together after the experimental work has been described.

a charge under one set of conditions until a certain end point was reached, if the distillation was interrupted for an hour or more and then continued under the same conditions as before, a further supply of oil could be obtained before the same end point was reached again. This additional amount of oil obtained as a result of interrupting the distillation amounted to from 2 per cent to 18.8 per cent of the oil already obtained before the distillation was interrupted. The highest increases in yields due to this manipulation were those runs where there was still considerable oil present in the wood when the distillation was interrupted (although, of course, all the oil possible had been removed under the prevailing conditions). For instance, in Runs 14 and 15, after all the oil possible had been distilled at 50 pounds pressure, interrup-

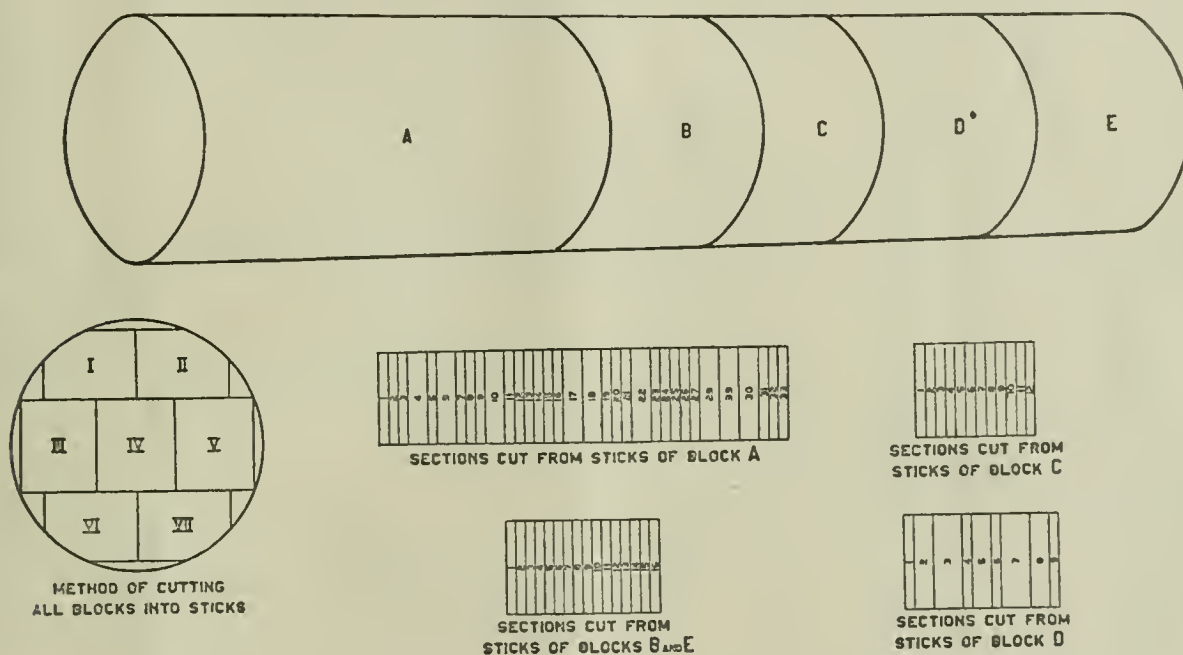


Fig. 2. Method of Selecting Materials.

End Point.—It will be noticed in Table II that the amount of oil in one liter of distillate gradually decreased and decreased very slowly toward the end of a distillation. On this account it became necessary to arbitrarily choose a ratio of oil to water which might be considered as the end of a distillation under one set of conditions in order to make the results of different distillations comparable and at the same time to keep the time required within practicable limits. In the first five runs the end point was too high and too variable, since it was not recognized that the end point must be very carefully regulated in order to obtain comparable results. These first five runs are, therefore, not comparable with those which follow, in which the end point was carefully regulated at somewhat lower values. It was also found that after distilling

tion of the distillations over night made it possible to distil respectively 18.8 per cent and 15.1 per cent more oil under the same conditions; in both these cases there was still considerable oil present in the wood as shown by further distillation at increased pressures. In Runs 11 and 21, however, after all the oil possible had been distilled at atmospheric pressure, interruption of the distillations made it possible to obtain only 2.9 per cent and 4.0 per cent more oil under the same conditions; in these cases there were much smaller quantities of oil left in the wood than in Runs 14 and 15. This effect also was not recognized as important until after Run 5 was finished, so that for another reason Runs 1 to 5 are not comparable with those which follow.

The proper end point for any distillation after Run

5 was considered to be reached only when the required ratio of oil to water in the distillate had been attained both before and after interruption of the distillation.

DISCUSSION OF RESULTS.

The data obtained by the distillation of the various runs are given in Table III, together with the conditions under which the distillations were made. In the table the size of the chip as given in column two is expressed in inches with the length parallel to the grain given first. The values given in the columns headed

TABLE II.—TYPICAL DATA SHEET, ILLUSTRATING THE RECORDS TAKEN OF THE DISTILLATIONS.

Project 123—Run No. 23. Chips. 1"×2"×2".									
Weight of can + water—				160 lbs.					
Weight of can + water + chips—				215 lbs.					
Weight of chips—				55 lbs.					
Steam turned on				9.23					
Distillate began to flow—				9.28.30					
Time.		Liters of distillate.	Cc. of oil in distillate.	Cc. of oil total computed.	Cc. of oil total determined.	Specific gravity of oil.	Pressure.		
Hrs.	Min.								
9	36	1	88	88	362	0.8810	70		
9	48	2	154	242		0.8794	72		
9	59½	3	110	352		0.8851	71		
10	8	4	73	425			71		
10	17	5	60	485			0.8944	68	
10	29½	6	55	540				71	
10	40½	7	50	590			0.8980	70	
10	51½	8	44	634				72	
11	½	9	39	673			0.8981	70	
11	8½	10	24	697				69	
11	18½	11	27	724		0.9010	72		
11	28	12	26	750			69		
11	38	13	19	769			72		
11	47½	14	22	791		0.9016	68		
11	57½	15	17	808			69		
12	7	16	17	825	839		69		
12	17	17	16	841			69		
12	27½	18	16	857			72		
12	38½	19	18	875		0.8987	72		
12	50	20	19	894			64		
1	0	21	15	909			71		
1	9	22	13	922		0.8965	72		
1	18½	23	11	933			71		
1	27½	24	10	943			69		
1	39	25	12	955	979		68		
1	48	26	10	965			70		
2	0	27	11	976			70		
2	11½	28	10	986			68		
2	23½	29	12	998		0.9858	72		
2	34½	30	8	1006			73		
2	45½	31	8	1016			72		
2	56½	32	10	1026	1047		63		
3	7½	33	13	1039			45		
3	17	34	6	1045			32		
3	26½	35	5	1050			20		
3	37	36	4	1054		0.8936	12		
3	43	37	1	1055			4		
3	45	38	1	1056	1095		0		
Distillation interrupted over night.									
9	23½	39	22	1078	}	0.8934	72		
9	35	40	17	1095			73		
9	46	41	15	1110			71		
							71		
9	57	42	10	1120	}	0.9003	72		
10	8	43	9	1129			70		
10	19	44	8	1137			72		
10	30	45	7	1143			58		
10	43	46	15	1158			34		
10	53	47	8	1166			19		
11	4	48	6	1172			0.8935	6	
11	6	49	2	1174				0	
No. of liters.		Yield cc. lb.		Efficiency.					
16		15.3		0.95					
25		17.8		0.71					
38		19.9		0.51					
49		22.4		0.46					

"yield" are expressed in cc. of oil per pound of wood. The possible error in these determinations of yields is apparently about 6 to 7 per cent and is due to difficulties in sampling, in regulating evaporation during the preparation of material, and in obtaining comparable end points in different distillations.

An example of results which must be due to such errors is seen in Runs 23 and 24. The chips in Run 24 are larger than those in Run 23 and the yield should be perhaps less and certainly not greater from the larger chips, and yet the yields obtained from Run 23 are 5.0 per cent less than those from Run 24. Another similar example is shown in Runs 30 and 31. It might be thought that some of these variations in yields were due to incomplete distillation caused by the "channeling" of the steam through the charge in such a way that part of the wood was never touched by the steam, but in several runs after all the oil possible had been distilled under some one set of conditions the top of the retort was removed, the charge well stirred, and the distillation continued under the same conditions as before without any indications that the stirring had discovered undistilled material in the charge. It seems probable, therefore, that with a retort of the shape and size used in these distillations, the effect of incomplete distillation due to incomplete contact between the steam and the surface of the chips is negligible.

The values given under "efficiency" are obtained by dividing the yields per pound of wood by the number of liters of total distillate, the efficiency factor being cubic centimeters of oil per pound of wood per liter cubic centimeters oil

of distillate or $\frac{\text{pounds wood} \times \text{liters distillate.}}{\text{cubic centimeters oil}}$

It might be thought that this "efficiency factor" would have more significance if it represented only the relation between oil and total distillate, but, as will be seen later,⁴ this relation would be affected by the amount of wood distilled. Of course, the effect may not be in exact proportion to the amount of wood distilled as represented in the factor used, but it is thought that more nearly comparable efficiency factors are obtained by including the amount of wood as above. These factors represent approximately the relative amounts of oil obtained in the different runs per unit of steam consumed, exclusive of the steam which supplies the heat lost by radiation.

EFFECT OF SIZE OF CHIP ON YIELD AND EFFICIENCY.

In general, other conditions being the same, the smaller the chip, the larger the yields and the higher the efficiency. This is shown in Table IV, which contains selected data from Table III. Four groups of distillations are given, in each of which all the other conditions except size of chip are as nearly as possible the same, and in every case the smaller-sized chips show the larger yield and higher efficiency. The effect

⁴The same reasoning as is given on page 794 regarding the effect of the size of retort on the efficiency applies also to the effect of the amount of wood distilled on the efficiency.

on yield is not so marked in the case of Runs 26 and 27 (and some of the other runs given in Table III), but this is accounted for by the fact that the pressure was high enough so that nearly all the oil was removed even from the larger-sized chips. In the case of two runs in which all the oil was removed even from the larger chips, the yields would of course be the same, but the efficiency would probably be higher with the smaller-sized chips.

EFFECT OF PRESSURE ON YIELD AND EFFICIENCY.

In general, other conditions being the same, higher pressures give larger yields without lowering the efficiency. This is shown in Table V, which gives three groups of runs, in each of which all conditions except steam pressure are as nearly as possible the same. In all cases the higher steam pressure produced the larger yield and with the same or higher efficiency. The effect of pressure on yields is also shown in another way in many of the runs in Table III, in which after obtaining all the oil possible by distilling under one pressure, a further yield of oil was obtained by continuing the distillation under a higher pressure.

EFFECT OF SPEED OF DISTILLATION ON YIELD AND EFFICIENCY.

Other conditions being the same, increased speed of distillation decreases both the yield and the efficiency. This is shown clearly in Table VI, which gives the results of two sets of two runs each, all the conditions except the speed being the same in each set. The more rapid passage of the steam through the charge probably causes it to be less saturated with the oil vapors, thus directly decreasing the efficiency. The yield is decreased probably because the same end point is reached sooner when the steam is less completely saturated. This is indicated by the more nearly equal total yields obtained in each set of runs by finishing up the distillations at the same pressure but at lower speeds. The variation in efficiency is not, however, as might be expected, exactly proportional to the speed, since doubling the speed decreases the efficiency by only about 10 per cent from 0.94 to 0.84 in Runs 30 and 31, and from 0.43 to 0.39 in Runs 32 and 33.

TABLE III.—SUMMARY RECORD OF EXPERIMENTAL RUNS.

Group	Run No.	Size of chips.	0 lbs. pressure.		20 and 30 lbs. pressure.		40 and 50 lbs. pressure.		70 lbs. pressure.		Total.		Speed, min. per liter.	End point, cc. per liter.
			Yield, cc. per lb.	Efficiency.	Yield, cc. per lb.	Efficiency.	Yield, cc. per lb.	Efficiency.	Yield, cc. per lb.	Efficiency.	Yield, cc. per lb.	Efficiency.		
I.	1	Sawdust	20.6	1.71			9.9 ^a	0.45			30.5	0.90	4	25 and 12
	2	Sawdust					32.7 ^a	1.26			32.7	1.26	4	18
	3	Sawdust	12.5	1.56			8.2 ^a	0.41			20.7	0.74	4	17 and 12
	4	2"×1"×1"							20.3	0.33	20.3	0.33	5	12
	5	2"×½"×¼"	6.4	0.61	5.8	0.45	3.9 ^a	0.33	9.1	0.33	25.2	0.38	4	12
	6	2"×½"×¼"	8.0	0.55	5.1	0.28	6.1 ^a	0.24			19.2	0.34	10	10
	7	1"×¼"×¼"	15.7	0.63	4.6 ^a	0.29	5.3 ^a	0.14			25.6	0.40	10	10
	8	1"×½"×¼"	10.2	0.46	6.5 ^a	0.25	6.2 ^a	0.19			23.0	0.29	10	10
	9	1"×½"×¼"			22.4 ^a	0.46	3.0 ^a	0.19	4.5	0.21	29.9	0.34	10	10
	10	1"×½"×¼"					27.2 ^a	0.46	1.5	0.12	28.7	0.40	10	10
II.	11	Sawdust	27.7	1.46			2.0 ^a	0.25			29.7	1.1	10	10
	12	1"×variable							25.7	0.49	25.7	0.49	10	10
III.	13	6"×variable							12.3	0.29	12.3	0.29	10	10
	14	1"×5"×8"					19.7 ^a	0.35	5.9	0.17	25.6	0.28	10	10
IV.	15	1"×½"×1½"					24.5 ^a	0.41	4.7	0.15	29.2	0.32	10	10
	16	Sawdust	25.2	0.97			4.0 ^a	0.31			29.1	0.75	10	10
	17	1"×¼"×¼"			24.5 ^a	0.50							10	10
	18	1"×¼"×¼"					26.8 ^a	0.50					10	10
V.	19	1"×½"×½"					25.3 ^a	0.55					10	10
	20	1"×½"×½"							29.8	0.63	29.8	0.63	10	10
	21	Sawdust	24.6	1.05			1.7 ^a	0.23			26.3	0.82	10	10
	22	1"×2"×2"							23.1	0.39	23.1	0.39	10	10
VI.	23	1"×2"×2"							22.4	0.46	22.4	0.46	10	10
	24	1"×4"×4"							23.6	0.44	23.8	0.44	10	10
	25	Sawdust	24.0	0.89			2.6 ^a	0.26			26.6	0.70	10	10
	26	1"×1"×1"							22.8	0.45	22.8	0.45	10	10
VII.	27	2"×1"×1"							21.4	0.31	21.4	0.31	10	10
	28	3"×1"×1"							12.9	0.29	12.9	0.29	10	10
	29	Sawdust	19.3	0.84			1.7 ^a	0.17			21.0	0.64	10	10
	30	Shavings	18.8	0.94									6	5
			0.6										10	7
			19.4	0.85									6 and 10	5 and 7
							3.1 ^a	0.39					10	10
											22.5	0.73	6 and 10	5 and 7
													3	5
			16.0	0.84									10	7
			1.4										3 and 10	5 and 7
			17.4	0.70			3.8 ^a	0.38					10	10
											21.2	0.60	3 and 10	5 and 7
									20.1	0.43			6	5
	32	1"×½"×½"							0.7				10	7
									20.8	0.39	20.8	0.39	6 and 10	5 and 7
									18.1	0.39			3	5
									2.2				10	7
	33	1"×½"×½"							20.3	0.33	20.3	0.33	3 and 10	5 and 7

^a=20 lbs. ^b=30 lbs. ^c=40 lbs. ^d=50 lbs.

TABLE IV.—EFFECT OF SIZE OF CHIP ON YIELD AND EFFICIENCY.

Run No.	Size of chip.	Pressures.	Yields.	Efficiency.	Speed, min. per liter.	End point, cc. distillate oil per liter
7	1"×¼"×⅛"	Atmospheric	15.7	0.63	10	10
8	1"×½"×⅛"		10.2	0.46		
12	1" sections from slabs		25.7	0.49		
13	6" sections from same	50 lbs.	12.3	0.29	10	10
14	1"×5"×8"		19.7	0.35		
15	1"×1½"×1½"		24.5	0.41		
26	1"×1"×1"	70 lbs.	22.8	0.45	10	10
27	2"×1"×1"		21.4	0.31		
28	2½"×1"×1"		12.9	0.29		

If, as seems probable, the effects of speed are due to the variations in the time during which the steam is in contact with the wood, then the size of the retort would have a similar effect, that is, a speed of 10 minutes per liter in a certain sized retort would be equivalent to 5 minutes per liter in a retort twice as large, since a unit of steam would be in contact with a unit of wood for the same length of time in either case.

RELATIONS BETWEEN END POINT, YIELD AND EFFICIENCY

As shown in Table II, the amount of oil in a liter of total distillate is greatest at the beginning of the distillation and decreases steadily as the distillation

TABLE V.—EFFECT OF PRESSURE ON YIELD AND EFFICIENCY.

Run No.	Size of chip.	Pressures.	Yields.	Efficiency.	Speed, min. per liter.	End point, cc. distillate oil per liter
8	1"×½"×¼"	Atmospheric	10.2	0.46	10	10
9	1"×½"×¼"	30 pounds	22.4	0.46	10	10
10	1"×½"×¼"	50 pounds	27.2	0.46	10	10
17	1"×¼"×⅛"	30 pounds	24.5	0.50	10	10
18	1"×¼"×⅛"	50 pounds	26.8	0.50	10	10
19	1"×½"×½"	50 pounds	25.3	0.55	10	10
20	1"×½"×½"	70 pounds	24.8	0.63	10	10

progresses, except when the conditions of distillation are changed, and then the increase in the amount of oil per liter is usually only slight and temporary. This was true in all the distillations and it is evident, therefore, that the efficiency factor will decrease steadily throughout the distillation and its final value will depend on the end point used. Therefore, the efficiency can be increased by stopping the distillation before all the oil possible has been obtained and thus decreasing the total yield of oil. For the same reason the efficiency will be decreased by continuing the

TABLE VI.—EFFECT OF SPEED ON YIELD AND EFFICIENCY.

Run No.	Size of material.	Pressure.	Speed, min. per liter.	End point, cc. oil per liter.	Yield.	Total yield.	Efficiency.
30	Shavings....	Atmospheric	6	5	18.8	18.8	0.94
		Atmospheric	10	7	0.6	19.4	0.85
		40 pounds	10	10	3.1	22.5	0.73
31	Shavings....	Atmospheric	3	5	16.0	16.0	0.84
		Atmospheric	10	7	1.4	17.4	0.70
		40 pounds	10	10	3.8	21.2	0.60
32	1"×½"×½"	70 pounds	6	5	20.1	20.1	0.43
			10	7	0.7	20.8	0.39
			3	5	18.1	18.1	0.39
33	1"×½"×½"	70 pounds	10	7	2.2	20.3	0.33

distillation until all the oil possible has been obtained and thus increasing the total yield of oil. For instance, in Run No. 23 (Table III) if the distillation had been stopped with an end point of 12 cc. per liter, at the 25th liter the yield would have been only 15.3 cc. per pound while the efficiency would have been 0.95. By continuing the distillation until the end point (after an interruption of the distillation) was 10 cc. per liter, a much larger yield, 22.4 cc. per pound, was obtained, but only at the expense of a much decreased efficiency (0.46).

THE PRESSURES REQUIRED TO DISTILL COMPLETELY DIFFERENT SIZES OF MATERIAL.

Sawdust.—The volatile oil cannot be completely distilled at atmospheric pressure even from a material as finely divided as sawdust. This can be seen from Runs 11, 16, 21, 25 and 29 (Table III) in which, after removing all the oil possible at atmospheric pressure, a further distillation at 40 pounds pressure removed from 6.6 to 15.8 per cent more oil. It was found that after distilling at 40 pounds pressure a further distillation at 70 pounds was without appreciable effect. It can be safely stated that 40 pounds pressure is sufficient for the removal of all the volatile oil from material as small as sawdust. It is possible that lower pressures might give almost as good results, but this point cannot be determined from the data on hand.

Chips 1"×¼"×⅛".—This size material cannot be completely distilled at 30 pounds pressure (Run 17) and probably not at 50 pounds pressure (Run 18). In Run 18 the yield obtained from chips 1"×¼"×⅛" is almost the same, within the limit of possible variation, as from the sawdust of Run 16, but apparently not quite all the oil has been removed.

Chips 1"×½"×½".—Chips of this size cannot be completely distilled at 50 pounds pressure (Run 19), but can at 70 pounds (Runs 20, 32, and 33).

Chips larger than 1"×½"×½".—At the maximum pressure used, 70 pounds, chips larger than 1"×½"×½" cannot be completely distilled, but as the size of chips is increased there is no sudden drop in the yield obtainable at this pressure until sizes larger than 2 inches with the grain (Runs 27 and 28)⁶ and 4 by 4 inches across the grain are used (Runs 14 and 24). It is probable that 80 to 85 per cent of the oil could be removed from chips 2"×4"×4" by distillation at 70 pounds pressure.

⁶In determining the percentage of total oil obtained in the runs of Group VI it must be remembered that the sawdust of Run 25 was not exactly a representative sample of the material of that group but that it was mixed with the sawdust obtained in cutting the slabs from the blocks. In several cases similar samples of sawdust obtained in cutting the slabs had been distilled and found to contain more volatile oil than the sawdust obtained in cutting the blocks. It is probable, therefore, that the proportion of volatile oil in the mixed sample of sawdust was somewhat greater than in the rest of the material in this group. This point is further indicated by a comparison of the yields obtained from the sawdust runs in the different groups. With the exception of Group VI (Run 25) the yields from the sawdust decrease, as might be expected, for the reason that the material for the groups was cut from the same log in order of the group number, beginning at the butt end and the content of volatile oil in the butt end was higher than in the upper portions of the log. It is probable, therefore, that a value of 24 to 25 cc. oil per pound of wood would more nearly represent the volatile oil content of the group.

EFFECT OF PRESSURE ON COMPOSITION OF OIL.

Analyses were made by the method described in Forest Service Bulletin 105 of part or all of the oil from each of the runs, but there was not enough difference between the various samples so that all of the analyses will need to be given. A few distillation curves showing the main points of interest will be given.

Pine Oil.—The proportion of pine oil in the crude turpentine did not vary except in cases which could be explained by variation in other factors besides pressure and, therefore, so far as the results show, the pressure has no influence on the proportion of pine oil except the influence due to increasing the total yields. In all cases where the total oil obtained was analyzed, and where the oil was nearly completely removed from the wood, the percentage of pine oil by weight varied only between 48 per cent and 52 per cent.⁶ In cases where only part of the oil was removed by the distillation, as in Run 4, the proportion of pine oil was less.

Dipentene.—The detection of small differences in the proportion of dipentene present cannot be made

dust mostly at atmospheric pressure (Fig. 3) apparently contains less dipentene than the oil distilled entirely at 60 pounds pressure (Fig. 4), the specific gravity values being lower and the proportion of the oil boiling between 165° and 180° larger in the latter case. It had formerly been thought that the dipentene which had been found on wood turpentines was caused by the temperature used in distilling the oil from the wood, but indications of dipentene were

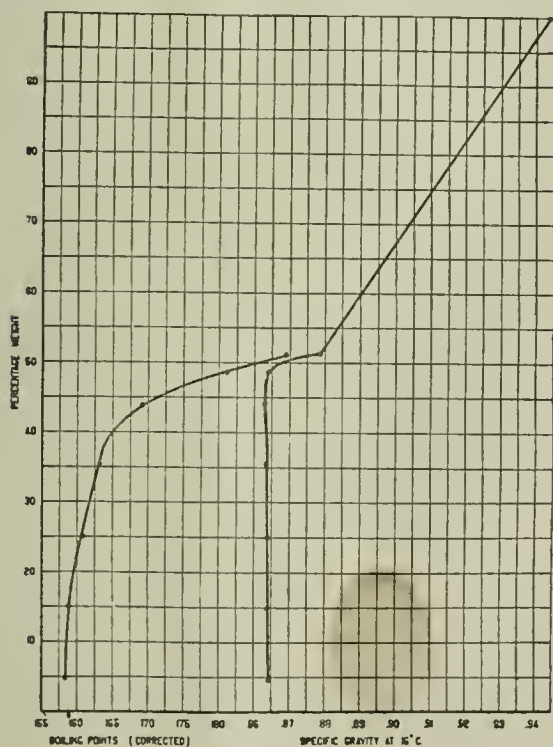


Fig. 3.

by the method of examination used, especially when such large proportions of pine oil are present. There seemed to be, however, more dipentene in the crude turpentines produced at higher pressures. Figs. 3 and 4, representing the distillation curves obtained in the analyses of the oils from Runs 21 and 23, respectively, illustrate this point. The oil obtained from saw-

⁶Exceptions were found to this in the oils from Group II which contained about 28 per cent pine oil. But the material for this group did not represent a complete cross section of the log, being composed instead only of the outside pieces, the slabs. The outer layers of this log evidently contained a smaller proportion of pine oil than the rest of the wood.

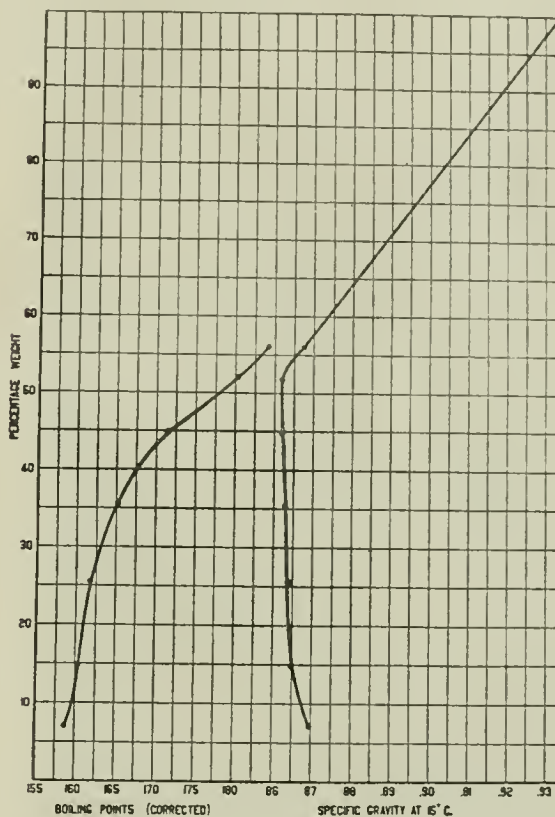


Fig. 4.

found in all the samples of oil obtained in this investigation, even in those produced at atmospheric pressure, and it is very probable that dipentene was present as such in the wood distilled. In order to make sure that this material with low specific gravity and high boiling point was dipentene and not some other terpene with similar physical properties, a chemical examination was made of the fractions 160° to 185° from some of the turpentines produced at atmospheric pressure and dipentene was identified by means of the tetrabromide, m. p. 125°-126°.

In order to determine the possibility of the transformation of pinene into dipentene under the condition of steam distillation the sawdust from Run 29 was air-dried and moistened with 1,175 cc. of gum turpentine (an amount equal to the total volatile oil originally present) and distilled at atmospheric pressure. The oil, on analysis, showed no indications of dipentene. The experiment was repeated, making the distillation at 50 pounds pressure, but with the same result. These results preclude the possibility of formation of dipentene from pinene under the con-

ditions of steam distillation pressures below 50 pounds and indicate very strongly that dipentene occurs as such in lightwood.

Light Oils.—Figs. 3 and 4 also illustrate another effect of pressure on the composition of the crude turpentines. In these analyses, as in many others, the crude turpentines produced at pressures as high as 70 pounds show a considerably higher value for the specific gravity of the first fraction than do the turpentines produced at lower pressures. This indicates that some substance with low boiling point and high gravity (above 0.870 at 15° C.) is produced at the higher pressures; this substance might come from the

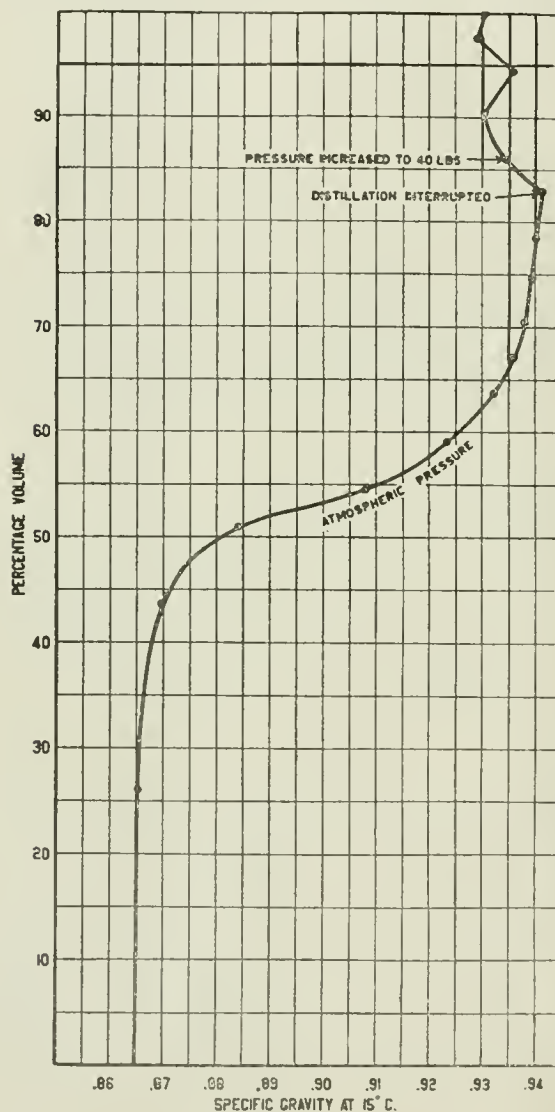


Fig. 5.

incipient decomposition of some portion of the resin at the temperature to which it is subjected. The first fractions from the analyses which contained this substance were slightly yellow and had a peculiar odor, different from the rest of the fractions. A treatment with caustic soda reduced the gravity of these fractions but increased the yellow color. It was found, however, that by the treatment of a turpentine like that shown in Fig. 4 with caustic soda followed by a distillation it was possible to prepare a refined tur-

pentine which showed no abnormality of the first fraction in color, odor, or gravity. The presence of this substance should not, therefore, introduce any difficulty in the refining process.

Another test for the presence of decomposition products was made on several of the samples produced at different pressures by treating the oil with

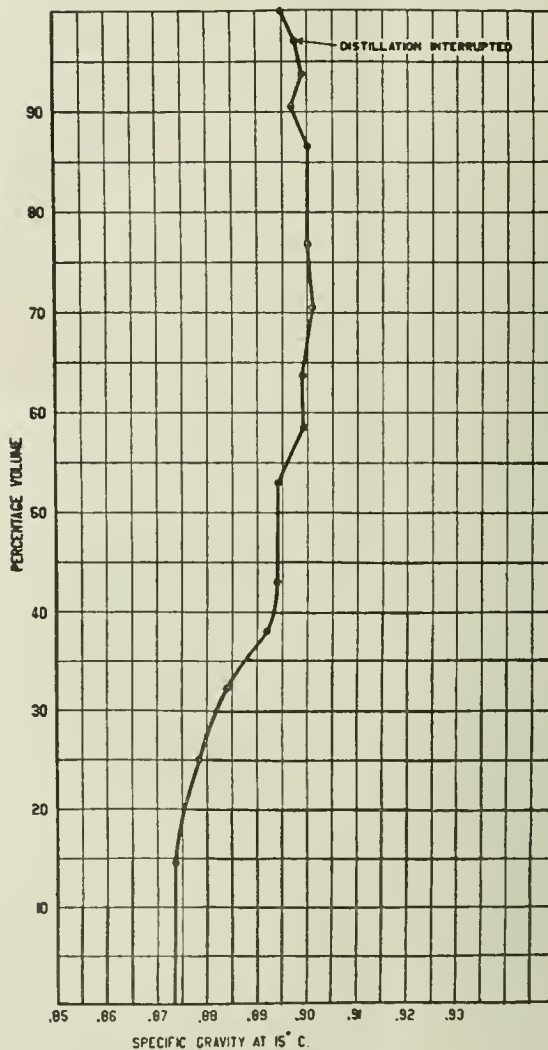


Fig. 6.

concentrated hydrochloric acid; a red color produced in this way is supposed to indicate the presence of rosin oil. There was only a very slight coloration of the oils produced at atmospheric pressure, but this coloration increased with the pressure, becoming very marked in the oils produced at 50 pounds and 70 pounds pressure.

FRACTIONATION OF THE OIL BURNING DISTILLATION.

Some very interesting conclusions regarding the details of the manner in which the volatile oil leaves the wood can be obtained by comparing the values of the specific gravity of various portions of the distillate. As was previously stated, the specific gravity of the oil was determined from each liter of distillate, or from as many liters as were necessary to furnish the amount of oil required for a determination. Figs. 5, 6 and 7 show these values of the specific

gravity obtained in Runs 16, 20 and 7, respectively, plotted against the percentages of the total oil obtained.

Fig. 5 shows the changes in the specific gravity of the oil obtained during the distillation of a charge of sawdust, first at atmospheric pressure and then at 40 pounds pressure. The first portions of the oil were nearly pure turpentine, but after about 44 per cent had been distilled the gravity increased rapidly, indicating the presence of pine oil in increasing quantities; when the distillation was from about 67 per cent to 83 per cent completed the oil was nearly pure pine oil. The part of the curve up to 83 per cent resembles very closely the distillation curve which could be obtained from the distillation with steam of a crude turpentine; that is, the presence of the wood seems to have no effect on the manner in which the volatile oils are distilled. A difference is seen, however, in that portion of the curve beyond 83 per cent; after practically all the oil possible had been removed by a continuous distillation at atmospheric pressure, the interruption of the distillation followed by a further distillation under the same pressure produced a small further yield of oil with a lower gravity, and on increasing the steam pressure, still more oil was obtained with a still lower gravity. This indicates that both the interruption of the distillation and the increase in steam pressure brought more oil into contact with the steam and that this oil contained some of the low-gravity turpentine material.

A very different behavior is shown in Fig. 6, which represents the distillation of chips $1'' \times \frac{1}{2}'' \times \frac{1}{2}''$ at a pressure of 70 pounds. In distillation under these conditions there was much less tendency for the oil to be separated as it is distilled, the gravity of the very first fraction being higher than that of pure turpentine and the gravity of the later fractions never reaching that of pure oil; that is, the turpentine and pine oil distilled together throughout the run. This indicates that new supplies of volatile oils were brought into contact with the steam more or less continuously throughout the distillation, since otherwise the turpentine would have distilled first and the last fractions would have been nearly pure pine oil.

A still more striking picture of the variation in the gravity of the distillate due to changes in the conditions of distillation is shown in Fig. 7; this represents the gravities of different parts of the oil obtained during the distillation of chips $1'' \times \frac{1}{4}'' \times \frac{1}{8}''$ at atmospheric, at 20 pounds, and then at 40 pounds pressure. During the first of the run at atmospheric pressure the gravity gradually increased, but never quite reached that of pure pine oil. By a continuous distillation at atmospheric pressure only about 50.5 per cent of the total oil could be removed, but on interrupting the distillation for about fourteen hours and continuing again at atmospheric pressure, 7 per cent more oil was obtained, the gravity of

the first part of this 7 per cent being much lower and of the last part only slightly lower than that of the last fraction of the continuous run. On increasing the pressure to 20 pounds, about 16.8 per cent more oil was obtained, the gravity suddenly dropping and then gradually rising during the distillation of this 16.8 per cent. On increasing the pressure to 40 pounds and distilling continuously, a further yield of 19.5 per cent was obtained, the gravity of this 19.5 per cent dropping suddenly at first and then gradually rising. A similar additional yield was obtained

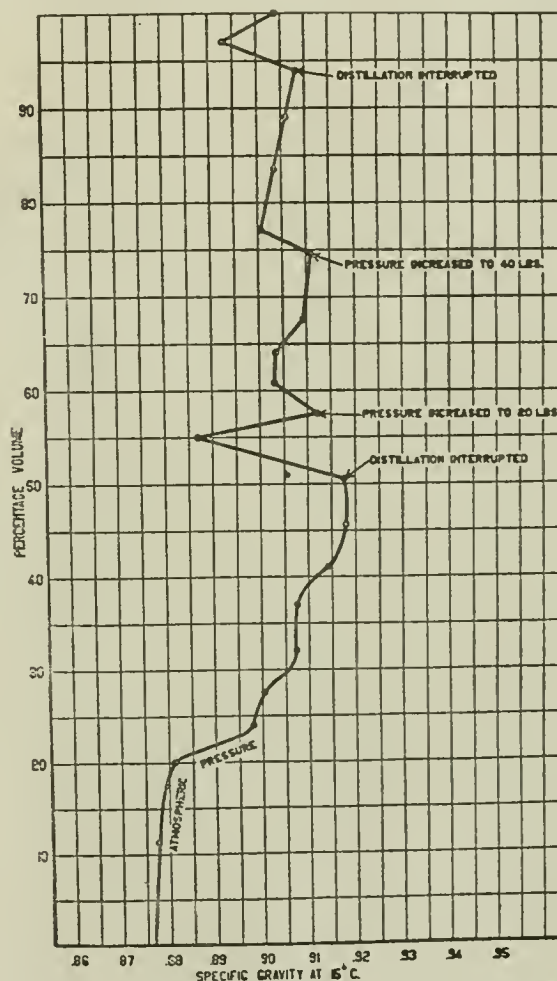


Fig. 7.

by another interruption of the distillation, about 6 per cent more oil being obtained.

Here again the effect of interrupting the distillation and of increasing the pressure are very plainly shown, viz., increased yield of oil with gravity lower than the last fraction obtained before the conditions were changed.

This effect of the increased pressure in increasing the yields is due then to bringing more steam and oil into contact with each other than is possible at lower pressures. This could result either from a penetration of the steam further into the wood at the higher pressures or from a flow of resin toward the surface of the wood due to the decreased viscosity at the higher temperatures. It seems probable that both

these have some influence, but the effect of the latter is quite certain, since it was noticeable that in the distillations made at high pressures a considerable amount of rosin would collect in the bottom of the retort or the outside of many of the chips would be coated with thin layers of rosin.

The effect due to the interruption of the distillation and continuing it again under the same conditions cannot be explained so readily, but it is probably due to a slow flow of rosin toward the surface or to the diffusion of the volatile oils in the rosin from the interior of the chip to the rosin at the surface from which the oil has been removed.

APPLICATION OF RESULTS.

The foregoing discussions have considered the effects of the different variables (1) size of chip, (2) pressure of steam, (3) speed of distillation, and (4) end point at which distillation is stopped, on (a) the yield of total oil, (b) the composition of the oil, and (c) the amount of steam required to remove the oil. It can be seen that there should be a certain combination of values for these variables which would give a most economical method of operation for a steam distillation plant; but there are other factors which must be taken into consideration in determining the proper combination of values. For instance, the best size of the chip will not be determined entirely by the effect of size on yield and efficiency, but also by the relative costs of preparing different-sized chips and the use to which the chips are to be put after steaming; the best pressure of steam will not be determined entirely by the effect of pressure on yield and efficiency, but also by the relative costs of high and low pressure steam and of apparatus designed for use with different pressures; the best speed for the distillation will not depend entirely upon the effect of speed on the yield of products and on the amount of steam required, but also upon the cost of steam and the overhead charges; the best end point at which to stop the distillation will not depend entirely upon the effect of end point on yield and efficiency, but also upon the cost of the raw material, the value of the products, etc.

Sufficient experimental data have been given, however, so that a knowledge of the various cost factors mentioned above (which would naturally vary a great deal in different plants) would make it possible to decide readily on the most economical methods for operating.

The mineral production of Iowa in 1913 reached a value of \$25,602,015, according to figures of the U. S. Geological Survey compiled in co-operation with the State Survey. This is an increase over 1912 of \$2,701,665. The two principal industries in the state are coal mining and clay working, which contribute nearly 80 per cent of the total.

THE CHEMICAL PULP INDUSTRY IN GERMANY.*

Three-fourths of the materials used for the manufacture of paper in Germany is obtained from wood and straw, only about 5 per cent consisting of rags. The total output of pure rag papers in Germany amounts to about 100,000 tons. About a hundred years ago, Germany's total production of papers amounted only to about one-fourth of the volume of rag paper now produced in that country and to one-hundredth of today's entire production for Germany. Inasmuch as in other countries the conditions are about the same as in Germany, and in part as regards the use of rags, even less favorable conditions prevail, it will be evident from these comparative figures that without the production of paper cheapening fibrous substances, it would be impossible to meet the present consumption of paper.

The separation and production in a technically pure form of the vegetable structural substance—cellulose—is designated as chemical pulp manufacture. Rag half-stuff might also be characterized in this way, but in a broader sense, the manufacture of cellulose is referred to as the separation of cellulose from wood, straw and varieties of grasses, and so when we speak of the manufacture of cellulose, we mean the production of chemical pulp from wood. This constitutes by far the most important branch of the cellulose industry.

The processes of manufacturing chemical pulp may be classified in three groups, accordingly as an acid, alkaline or neutral disintegration process is used. Wood consists principally of the carbohydrate cellulose, a saturated combination, and a solid, gelatinous colloid. In addition, there is present in wood lignin which represents the lignification of the actual plant forming substance. In the separation of the cellulose from the wood, that is in wood cooking, the lignin splits off and is transformed into soluble combinations, in which it is not only simply dissolved, but in all probability hydrolytically decomposed. Characteristic and determinative of the correctness of a cellulose cooking process is not only the possibility of separating the cellulose, and removing the lignin but the removal, undecomposed, of the soluble product obtained; for should a decomposition of the lignin, or the soluble products formed from it be effected by oxidation or dehydration, substances difficult of solution might be formed which would so contaminate the cellulose as to make it no longer fit for use.

The chemicals used to separate the cellulose from the wood substance are employed in liquid form and at high temperature. The cellulose can be obtained,

*Before the Educational Section of the Austro-Hungarian Society of Cellulose and Paper Chemists in Vienna, last March, Dr. Arthur Klein read a paper on "Progress in the Cellulose Industry," which was published serially in the *Papierfabrikant*, beginning with the issue for May 22, 1914. The accompanying is a translation made especially for Paper and is reprinted here from that journal.

by the action of either neutral, alkaline or raw acid cooking solutions. As neutral cooking solutions, hot water and neutral sulphide solutions are recommended.

The alkaline solvents are used in the form of aqueous solutions of alkalis, chiefly sodium hydroxide and sodium carbonate, also of alkaline sulphide solutions and mixtures of both.

Acid cooking solutions are recommended for the actual acid processes in which nitric acid, nitromuriatic acid, hydrochloric acid and sulphurous acid have found employment. The generally used and most important industrial process is, however, the acid process in which solutions of bisulphite of lime and magnesia are used.

Of all the processes three have persisted for use on a large scale: two alkaline soda processes, in which either aqueous alkalis, or mixtures of these with sulphate solutions (the soda and sulphate processes), and an acid process, the sulphite process.

Wood, the raw material of cellulose manufacture, is by no means scarce in nature. According to Uhlmann, forests cover 30.9 per cent of northwestern Europe, 16.1 per cent of southwestern Europe and 38 per cent of eastern Europe, giving for all Europe about 38 per cent of forest area. Of the woods it must be admitted that so far a comparatively small proportion have been utilized in cellulose production. At present but few of the leaf woods, mostly the needle woods and even of the 340 varieties of taxaceæ, hardly any but the abieaceæ have been used. In Europe only the fir or red pine (*Pinus abies*), white or genuine pine (*Pinus pecea*), fir (*Pinus sylvestris*), and in addition to these, more rarely some of the varieties of beech (*Fagus*), poplar (*Populus alba* and *Italica*) and others. In America, spruce (*Picea nigra*), hemlock (*Tsuga canadensis*), white and gray pine (*Pinus canadensis*) and in smaller quantity, poplar and aspen (*Populus grandidenta* and *tremuloides*) in addition to other but very little used species of wood have been employed.

When we take into consideration, as an index of the progress made in the use of wood for cellulose production, the statements made by Mitscherlich for his licenses, we find that he of course preferred, above all, white pine, and next to that needle pine as first class material. The employment of fir and larch and some leaf woods was only introduced later.

In consequence of the increasing use of wood in building and mining industries and other branches of manufacture outside of the paper industry, the requirements as to quality made in regard to wood, have undergone material modifications in the course of time.

If we put the production of cellulose in the year 1913 at 4,000,000 tons, this means a consumption of wood for cellulose manufacture of about 20,000,000 cubic meters; for mechanical pulp we can calculate 13,000,000, and for card and box board another 3,000,000 will be used, so that for the paper industry in

1913, 33,000,000 cubic meters of wood would be consumed.

The consumption of wood has developed with extraordinary rapidity during the past sixty years and this has resulted in twigs, branches and saw mill refuse, also known as outside slabs, finding their way into the chemical pulp mills. That this has not proved injurious to the strength of the cellulose produced therefrom is proved by calculations made by Sutermeister in the accompanying table:

Inches.	Kind of wood.	Length of fiber in Mm.	Thickness in Mm.	Length and thickness in Mm.
3	heart	0.49	0.015	32.7
3	outside	0.85	0.018	47.2
9	heart	0.75	0.017	44.1
9	central portion	1.00	0.023	43.5
9	outside	1.09	0.024	45.4

From the figures cited it may be gathered that the outside wood contains longer and thicker fibers than the heart. Inasmuch as for an equal quantity of cellulose made from thin wood, more outside wood will be used, it stands to reason that the wood fibers which make up the bulk of a given quantity of cellulose from thin wood are longer than were the fibers from the thicker wood formerly employed in the production of an equal quantity of cellulose.

According to modern methods of utilizing wood, we recognize the certainty with which large or small differences in the raw material can be equalized in the subsequent manufacture. Mitscherlich, in his confidential circular, advises the use of wood as freshly cut as possible for cooking and if nothing but dry wood is to be had for use, to sprinkle it for a few days or put it in water and allow it to lie there several days. These are conditions that on the large scale of modern operations could not possibly be complied with, seeing that the Mitscherlich plants of originally 2,000 kilos daily capacity have given place to the extensive operations of our times. Mitscherlich's rule that fir and pine woods be worked separately can also no longer be complied with and large plants must equalize these differences by other, better arrangements.

The waste that was formerly unavoidable with Mitscherlich's method of boring out roots and barking, amounting to 20 per cent and which, by sawing the wood into disks of 3 cm. in thickness, caused a further loss of 10 to 20 per cent, has been considerably reduced, because at present, in the barking of round wood by hand, it does not amount to more than 6 to 7 per cent and with mechanical barking to more than 10 to 12 per cent, while the cutting into disks is altogether abolished and in place of this we have the chopping machines, of which the first was produced in the '70s by James A. Lee and which worked practically without loss. The wood mills, built on the plan of a coffee-mill, have likewise entirely disappeared while the centrifugal mill, also known as a disintegrator, invented by Carr in 1862, is now used almost universally by cellulose manufacturers.

To refer more particularly to the different types of chopping machines, centrifugal mills, wood grinders, and the mechanical transportation devices employed, would here be out of place. It must, however, be noted, that in many districts where there are large saw mills, the system of using the saw mill refuse or side slabs, that was used in the manufacture of soda pulp, is now used also by sulphite mills, where wood cut in summer that is free from bark and bast is available, whereas saw mill refuse, including bark, cannot be used for sulphite cellulose. The brown spots, which are not eliminated by bleaching, lower the value of sulphite cellulose. Various suggestions have been made in regard to the wet preparation of pieces to which bark is attached, but the wet preparation of the wood is very undesirable in subsequent cellulose cooking, because, either a very long preliminary steaming of the stock for boiling is required or the cooking lye must be of 70 Be, as in the old Mitscherlich process and the cooking must proceed very slowly. The barking drums recommended by Bache-Wiig, in which the wood comes in contact with steam, promise better results. In these drums, owing to the difference in swelling between wood and bark, the particles of wood, by passing over stationary slats in the revolving drum, are set free. In this case, too, the disadvantages of the wet preparation occur only to a limited extent.

The preliminary preparation of the wood does not differ in either the alkaline or the acid process of cooking as these are conducted at the present time. In the soda process the possible presence of iron in the mill water supply is of little or no consequence, but it is a very troublesome factor in sulphite manufacture, as it causes the bleached stuff to turn yellow, even if only traces of iron are retained on the fibers, while an unpleasant gray inklike tint interferes with the production of brilliant shades in colored papers made from unbleached sulphite. The unsightly gray-black muddiness which develops in sulphite cellulose is caused by the combination of the iron with a tannin found in the cooking lye, which forms a sort of inky varnish that is precipitated on the fibers.

Other dissolved impurities in the water, so long as the percentage is not abnormally high, are not so troublesome in the manufacturing process. More objectionable are the mechanical impurities, consisting of undissolved particles of bast, and also the apparently dissolved substances which are known as colloid solvents and which impart to the raw water its opalescence or turbid transparency.

It is not difficult to purify such waters, whether they carry these impurities with them constantly or only intermittently, the colloid solvents causing the greatest difficulty. However, it is also possible to remove these colloid substances without great trouble. The remedy consists in the introduction of an electrolyte into the water and the use of mechanical con-

trivances so as to produce a copious precipitate, whereby it is possible with the aid of subsequent filtration, to obtain a perfectly clear water.

If, returning to cellulose production proper, we consider the yield from the raw material by the sulphite process and the soda process, we find that Rosenhein arrived at a 25 per cent yield from the wood, Faudel 22 per cent, Ungerer about 35 per cent and Eckmann about 33 per cent. Mitscherlich claimed at first a somewhat similar yield to Eckmann which, however, at the beginning of the nineties, according to Harpf's figures, was raised to more than 40 to 42 per cent, whereas today we obtain from the sulphite process 45 to 48 per cent yield, from the sulphate process 35 to 38 per cent and from the soda process 30 to 38 per cent. This improvement in the yield is due in part to the better utilization of the wood in preparation, but it is also in large part attributable to changes in the cooking process itself.

If we consider again the secret directions for the sulphite process, as regards cooking, given by Mitscherlich, we shall find that for 2 cubic meters of digester contents one cubic meter of fir wood is treated with 7° lye and it is required that with 6° lye one-seventh less wood be used. From this therefore we can calculate that there is a yield of 60 to 65 kilos of cellulose per cubic meter of digester contents, since there was a loss of 40 per cent in barking and sawing. Mitscherlich rightly recognized that below 110° C. the lye had no effect on the wood. In his cookings, however, it took twelve hours before 110° was reached.

This temperature of 110° is then maintained for twelve hours, boiling up to 117°, the ammonia test being used continuously to control the cooking. The cookings consequently last at least thirty-six to forty-eight hours, during which a temperature of 117° is reached as a maximum. Eckmann, who in English patent No. 3,032 secured, in 1881, protection for sulphite of magnesia as dissolving or disintegrating medium and for a waste gas valve, used vertical cookers with steam jacket, whereby after seven hours he reached 4.5 atmos. and after nine hours 6 to 6¼ atmos. and at this pressure remained stationary for one to three hours, so that he finished cooking in ten to twelve hours cooking time. Kellner brought his cooker in 1½ hours to 105°, heated further to 109° and allowed to stand for three hours, to again increase the temperature to 125° to 138°. With about eighteen to twenty hours' boiling time he obtained a cycle of twenty to thirty-nine hours, which, as compared with Mitscherlich, indicated a considerable increase in the output per unit of cooker capacity. At the present time, even what are known as Mitscherlich mills do not follow Mitscherlich's directions as to cooking and the general high temperature maintained by them borders on 125° to 130° C., while the pressure in the cookers amounts to 2.5 to 4.5 atmos. whereby not alone the temperature in the cooker is dependent on

the pressure, but also the volume of free sulphurous acid present in the digester liquor during the cooking.

The Ritter-Kellner mills, that is, those that work only with direct heat, take 5 to 6 atmos. in pressure and in temperature go up above 140°C ., while the total cooking period is nine to ten hours throughout, only rarely more. After having established by titration with iodine an objective standard for the course of the reaction in cooking and advanced experience, by trying the odor and color of the boiling lye permits a fairly correct estimate of the condition of the cooking process, so that its management is today no longer a matter of difficulty.

Regarding the collateral operations in cooking, it may be pointed out that the loose charging of the wood in the digester has long been superseded; stamping it in by pneumatic stampers, copied from other industries, now being used for this purpose. It has been found possible to increase the yield by over 85 kilos, which was considered, until a few days ago, a good average for the cubic meter net digester capacity, whereas today 90 to 95 kilos per cubic meter net digester capacity is attained. An abbreviation of the cooking process was effected by blowing out the stuff, as practised in the fifties in soda cellulose plants and subsequently recommended by Kellner, or by washing out as was already known to Mitscherlich.

Inasmuch as the charging of the digester with lye is effected much more rapidly now-a-days than formerly and the steaming recommended by Haskell, as early as 1867, is frequently omitted, it is usually possible to reduce the period of digestion to twelve to twenty hours, the size of the digester of course, having to be taken into consideration, for, as we shall see, the charging and introduction of the lye depends upon this. It stands to reason that a digester of 80 to 90 cubic meters requires less time for charging, etc., than the large cookers, which are often constructed of a capacity of 350 cubic meters, although in production unit, the latter offer the greatest advantage.

The digester forms seen in modern sulphite plants vary considerably, but generally speaking we may say that today more upright cookers are built. Personally, I know of but one case where, in the erection of a new plant in Germany, within the past fifteen years, horizontal digesters have been installed.

The improvements in masonry effected of late years may be briefly summed up as follows: The knowledge that cement and iron have nearly the same coefficients of expansion has been turned to good account, and iron, lined on the inside directly with cement, has been used, and this has been followed by lining with acidproof tiles. The qualitatively better productions of the clay industry have played an important part in this advance, while the empirical knowledge possessed by cellulose technologists has enabled them to keep the masonry lining light. It was found that digester

liquor that penetrated into the masonry was speedily transformed into gypsum and thereafter formed the best protection against penetration of the liquor, provided that the first digester liquor penetrating to the iron was prevented from exuding. Apparently at the spot where the digester liquor encountered the iron jacket, there was formed a concentrated iron solution which protected the iron against further corrosion; after this there might be a chemical decomposition with the formation of insoluble iron calcium sulphite which would protect the iron against further corrosive action.

One of the most important operations in the manufacture of sulphite cellulose is the preparation of the liquor. In this operation the general preference that the cooking should be done with much free acid must be taken into consideration. Mitscherlich has solved the production of sulphite liquor in a technologically perfect manner, which is proved by the fact that at present more and more plants are installing the high sulphite towers introduced by Mitscherlich and his licenses and that comparatively little use is made of other methods of manufacturing sulphite liquor. The principle of every installation of this kind that shall work well is the obtaining of the greatest possible absorption surface and a good preliminary cooling of the gas.

In the preparation of sulphite acid, the absorbing liquid is either maintained stationary and the sulphurous gases to be absorbed conducted through it, as is the case in most lime emulsion sulphite liquors, or the absorbing liquid and the current of gas are brought into contact with one another on the counter-current principle, as for instance in the tower systems, or the lime emulsion, atomized, is conducted in the opposite direction into the gas current.

According to type, the sulphite acid plants come under two classes, the tower and the tank system. In the first, limestone or dolomite is employed; in the latter, limestone, dolomite or lime emulsion. The tank system again may either be continuous, as for instance the Kellner system with limestone, or one of the many lime emulsion processes, such as Partington (pressure), Behrend (suction), Stebbins and others, or the tank system may work intermittently as recommended by Frank, who provides for occasional overflow from one tub to another.

The movement of the gas is effected by absorption and stock draught in towers or by the exhaust effect of a fan or injector or finally by compressor action under pressure.

The SO_2 gases which are obtained from sulphur pyrite, always contain SO_3 , because the Fe_2O_3 exerts a catalytic action. According to Lunge there are present in 94 volumetric per cent of SO_2 6 per cent of SO_3 , but this volume of SO_3 may of course be much greater in case the furnaces run hot or sublimation occurs.

The calcination gases produced from sulphur also contain some SO_3 but with proper working this loss is infinitesimal.

The SO_3 in the calcination gas is of course consumed by lime and is lost for manufacturing purposes.

To the development of polythionic acids and their injurious effect Mitscherlich has already directed attention and recently Klason has also recognized selenium in the sulphite liquor as injurious to the cookings.

The roasting out of sulphur pyrite is accomplished frequently in the mechanical furnaces, such as are used in the sulphuric acid industry and which are built according to the systems of Herreshoff, Kauffmann and others.

Many sulphite plants have of late installed rotary sulphur burners, which of course, as regards surface, produce much more than the flat, stationary burners, because a new sulphur layer is constantly presented to the oxidizing air.

Briefly enumerated, the progress made in sulphite liquor preparation shows: (1) rational management of the roasting process and avoidance of excessive oxidation losses; (2) artificial draught and better preliminary cooking of the gas, whereby the production of liquors of desired strength is made possible independent of weather conditions. The preliminary cooking of the gas is not only necessary on account of better absorption but also because, in alkaline solution, at high temperature, considerable oxidation takes place.

The consumption figures in the old plants, sometimes rose, according to Schulte, to 90 kilos of pyrite, while 40 to 45 kilos of pyrite or 18 to 20 kilos and upward of sulphur was quite common. Today this is reduced to 25 to 26 of pyrite and 10 to 11 of sulphur to 100 kilos of unbleached cellulose obtained.

Necas gives 20 to 45 per cent recovery and many plants for a long time past have recovered an average of 35 per cent. Kellner, above all others, from the beginning, devoted particular attention to this recovery and before him Ekman already obtained a patent on spent gas valves. The digester waste gas contains, in addition to SO_2 , organic acids, which are the cause of their peculiar pungent odor. The green color of sulphite liquor obtained from waste gases is also to be ascribed to this cause.

Generally speaking, the work should be so conducted as to condense as much as possible from the waste gases, this, condensation, consisting chiefly of liquid SO_2 serves for the enrichment of the cooking liquor, while the surplus gases are collected in the ordinary absorption receptacles, or in specially constructed containers.

The two alkali processes of manufacturing chemical pulp have long since been surpassed in quantitative efficiency by the sulphite process.

The older soda process was brought out in 1853 by Watt and Burgess, in which about $5\frac{1}{2}$ per cent NaOH solution was used. The pressure amounted to $4\frac{1}{2}$ at-

mospheres. Upright digesters were used, and the stuff was blown out.

Some years later Houghton used horizontal digesters and a solution of caustic soda of about 5 per cent strength, under a pressure of 10 to 12 atmospheres, that is, about 180°C .

Lee and Dresel also worked like Houghton, only the digesters were externally directly fired. Such digesters remain in use only in five plants. Sinclair used digesters having perforated inner bottoms under which the heating steam was led. Among the later changes is the interesting process of Ungerer, who employed a battery of digesters operated on the counter-current principle.

Strictly soda cellulose plants steadily become fewer because the new method, the sulphate process, yields a whiter, more flexible and cheaper cellulose, and the yield from the wood is better.

Some pulp mills employ rotary digesters, some blowout digesters, with forced cooker lye circulation, such as are recommended for the sulphite process, but modern plants favor the dumping cooker, with direct steam heating. The largest dumping digester of which I have knowledge, constructed of one welded piece, has a capacity of 45 cubic meters.

In 1861 Henry used 10 per cent Na_2S solution for disintegrating; in 1867 Biron recommended alkali and lime sulphide; in 1871 Eaton used 2 and 6 per cent Na_2S solutions.

Helbig, in 1882 employed 7 per cent Na_2S solution for disintegration. The Dahl process was introduced in 1884. In this process sodium sulphate was employed to replace soda salts lost in the process. Sodium sulphide was thus produced by reduction through the action of organic carbon originating in the wood, and the cooker lyes consequently represent a mixture of different soda salts. This sulphate process from the soda process differs only in the composition of the lye.

The soda cellulose plants worked with cooker lyes of 6° to 14° Baumé, in which 75 to 85 per cent of the soda salts are caustic, the remainder being present as carbonate.

In the sulphate process different lyes are employed. One high class plant uses, for instance, the following composition: 1.5 per cent Na_2CO_3 ; 6.2 per cent NaOH ; 2.2 per cent Na_2S ; 0.4 per cent Na_2SO_4 ; 0.3 per cent Na_2SO_3 . Pressure up to 8 atmospheres, temperature ordinarily 160°C .

All the coke made in New York is made in retort ovens from coal mined in Pennsylvania. There are four establishments in the state, with a total of 555 ovens. Although New York lies entirely outside of the coal-producing area, it was the first state in which were built by-product ovens, which save the gas, tar, ammonia, etc. The first 12 Semet-Solvay ovens constructed in the United States were erected in 1893 at Solvay.

THE LABORATORY

SCRUBBER FOR CHEMICAL LABORATORY VACUUM SYSTEM.*

By CHARLES BASKERVILLE.

In order to protect the vacuum pump of our laboratory from the corrosive action of the gases drawn therein, I devised the installation described herewith. The pump—An improved Packard Vacuum Pump, 2 cylinder, 12 in. diam., motor-belt driven—has been in more or less continuous service for seven years without any expenditure thereon for repairs, as a result of this protection. It seemed safe, therefore, to present an account of it.

The installation is an application of the simple principles usually applied on a small scale with glass apparatus in the laboratory.

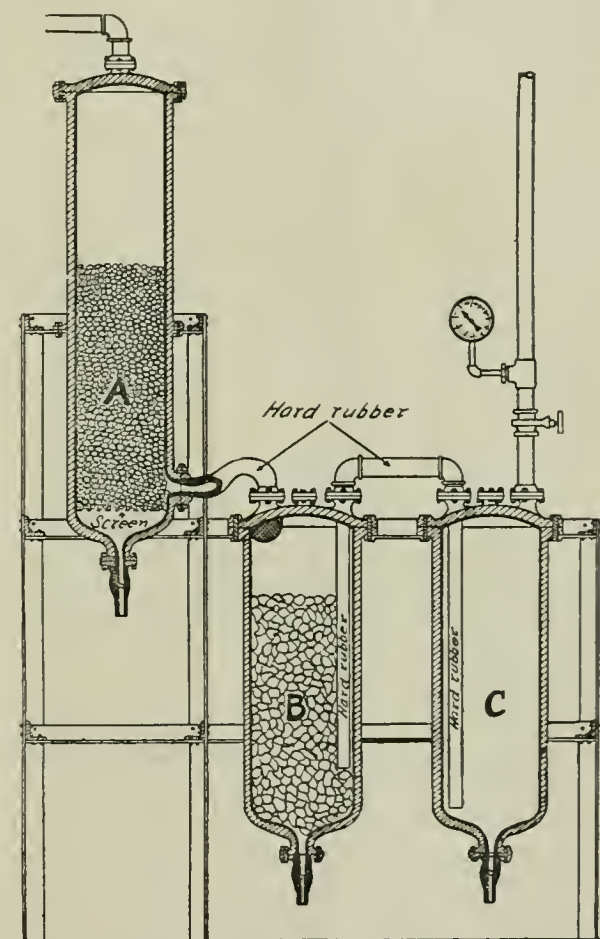
The towers are made of cast iron, porcelain-lined, and set into the system with a by-pass, which we have used only during the short time necessary for recharging. The towers are connected by hard rubber pipes (2 in. internal diameter). At the bottom of each tower is a hard rubber drain cock, bolted to a flange. At the top of *B* and *C* are plates bolted to flanges, which may easily be removed. The opening is of sufficient size to admit dropping a strung incandescent bulb for inspection.

Tower *B* is three-quarters filled with pumice stone in egg-size pieces. The pumice is thoroughly saturated with concentrated sulphuric acid. I believe lead pipe would be better in this cylinder as the hard rubber softened on contact with the acid. So far, however, the weight of the pumice and acid has not been sufficient to cause the hard rubber pipe to collapse. The decomposition of the rubber compound became so pronounced with the drain cock in a short while that it was replaced by a lead plate, which has proven satisfactory. Incidentally, it may be stated that all efforts to get the hard rubber people to provide a material which would stand up against cold concentrated sulphuric acid have been futile. Hence, it may be well to warn others as to their claims in this respect. A pear-shaped screen of copper gauze was placed in the opening of Tower *B* leading to Tower *A* to prevent clogging, in the event a rushing action of the pump sucked pieces of the pumice. We draw off and replenish the acid once or twice a year.

Tower *A* is half filled with angular pieces of commercial caustic soda, in size from a hazel nut to an

egg. The mass rests upon a copper wire gauze screen supported on and by the tapering bottom of the tower. The drain cock admits of drawing off any liquefied caustic which may accumulate. A metal pipe leads from the top to the pump.

Tower *C* is a safety reservoir to catch the fluid from *B* in the event of a leak beyond or other cause



Scrubber for Chemical Laboratory, Vacuum System.

A—Caustic Soda; B—Sulfuric Acid and Pumice; C—Trap.

for increase in pressure on the pump side in the line. So far, no indication of its real need has been apparent, as the maximum and minimum contacts of the automatic regulator of the motor have never failed.

A gauge in the system beyond the scrubber serves, by comparison with the gauge on the pump, to show leaks in the scrubber. None was observed until the hard rubber drain cock on Tower *B* failed, and none has been noted since the change described above, over six years ago.

The whole installation is supported on angle iron,

*Presented at the 6th Semi-annual Meeting of the American Institute of Chemical Engineers, Troy, New York, June 17-20, 1914.

painted with a rust-proof paint and may be inspected by members of the institute any time.

STUDIES ON FILTRATION.*

By J. W. BAIN and A. E. WIGLE.

In connection with factory operation quite recently, one of the authors had to form an estimate, in advance, of the amount of moisture which would be retained by a finely divided solid on a vacuum filter. A search among the usual sources of information yielded no serviceable data. When the filters were in actual operation, their performance in this respect was very much better than had been anticipated, and had this fact been known in advance some economy in construction might have been effected.

With a view to gaining information on this point, the authors investigated the literature at their disposal, and with the exception of the interesting and valuable paper by Hatschek they were unable to find any useful data. When the experimental work had progressed to a certain extent, an accident drew our attention to the exhaustive monograph of King and Slichter, "Principles and Conditions of the Movements of Ground Waters," from which we have drawn freely in this discussion.

In the problem which is here under investigation, the solid is assumed to be bathed by a liquid in which it is insoluble, such as, for instance, the mother liquor of a crystalline magma. It is proposed, therefore, to investigate the amount of liquid retained by a mass of finely divided solid when filtration is carried out under atmospheric or other pressure and also in the centrifuge.

The experimental work was considerably simplified by the condition laid down above, which permitted the use of a solid insoluble in water. A quantity of pure well-rounded lake sand was carefully sieved, and the grains which were retained on the 40 mesh screen but which passed the 30 mesh, are referred to throughout as 40 mesh sand. The screens used were not of very good quality in the regularity of the mesh opening, as will be seen from the data given later, but this point is of no particular significance in this investigation.

The rate of flow of a given liquid under a constant head through a filter-mass of a finely divided solid will obviously be dependent upon the amount of space which is not occupied by the grains, *i. e.*, what is commonly called the "pore space." On first consideration, it would appear that the pore space would

vary a good deal according to the size of the grains composing the mass, and the results of computation and experiment are an astonishing contradiction to this idea. The pore space is almost independent of the size of the grains, and the arrangement of the latter is of chief importance. By considering a number of small spheres of uniform diameter packed as closely as possible in a given space, it is possible to arrive at a mathematical formula from which the pore space may readily be calculated.

Slichter³ has shown that if the spheres are so arranged that their centers lie at the corners of a cube, the pore space will be 47.64 per cent; while if the centers of the spheres lie at the corners of a rhombohedron which permits the closest possible packing, the pore space is 25.95 per cent. Between these limits we may expect to find the porosities of all ordinary materials.

With actual materials, in the case where the grains are of approximately equal size, the pore space and also the diameter of the particles may be readily determined by counting a number of the grains, determining their combined weight and the specific gravity of the material: the total volume may be ascertained by adding the sand in small quantities to a cylinder, tapping gently with a flat-faced pestle until no further decrease in volume takes place. The results of this procedure on our sands are presented in Table I:

TABLE I.

Mesh screen.	No. of grains.	Total wt. grm.	One grain grm. $\times 10^{-3}$.	Sp. gravity.	Pore space per cent.	Diam. Mm.
30	{ 300	0.0307	10.23	2.74	35.4	0.420
	{ 300	0.0316	10.36			
40	{ 400	0.0251	6.3	2.68	34.1	0.354
	{ 400	0.0253	6.3			
50	{ 400	0.0182	4.55	2.73	36.4	0.318
	{ 500	0.0246	4.92			
60	{ 800	0.0238	2.97	2.82	36.8	0.269
	{ 600	0.0172	2.87			
80	{ 800	0.0202	2.52	2.85	37.7	0.257
	{ 600	0.0156	2.60			

The comparatively slight variation in pore space is worthy of note; and it may be added at this point that mixtures of small and large grains show a surprising similarity in their porosity to that of either taken alone. For all practical purposes, the pore space of masses of crystals, such as are commonly produced by rapid cooling, may be placed at 37 per cent of the total volume occupied.

FILTRATION UNDER ATMOSPHERIC PRESSURE.

This part of the subject has been so carefully worked out by King⁴ that it suffices to reproduce some of the results, slightly modified to suit the present purpose. Cylinders 8 ft. long, 5 ins. in diameter, were filled with special, sorted sands, wire gauze being used as a support at the bottom. Water was introduced from below, and when the tubes were full, percolation

*Paper presented at the 6th Semi-annual Meeting of the American Institute of Chemical Engineers, Troy, New York, June 17-20, 1914, and reprinted in the Journal of Industrial and Engineering Chemistry.

¹J. Soc. Chem. Ind., 1908, p. 538.

²Nineteenth Ann. Report, U. S. Geol. Survey.

³Loc. cit., p. 309.

was allowed to commence, and the water which drained away was collected and weighed at intervals.

TABLE II.

Effective size of grains. Mm.	Pore space. Per cent.	Water retained—per cent of dry sand.	
		After 1 hour.	After 9 days.
0.4745	38.86	11.23	4.24
0.1848	40.06	12.72	5.05
0.1551	40.76	14.73	7.25
0.1183	40.57	19.30	9.41
0.0826	39.77	20.15	11.82

FILTRATION WITH VACUUM.

Experiments were carried out by the authors with the idea of approximating to factory conditions.

The sand was poured into a Buchner funnel provided with a piece of wire gauze, and gently tamped down with a flat-faced pestle; the depth of the layer was $1\frac{1}{4}$ ins. The top of the funnel was closed by a glass plate ground to fit and provided with a central aperture through which air could be admitted. To avoid the error of surface evaporation during filtration, this air was drawn through a tower, down which water trickled slowly. The funnel was placed in a suction flask and a simple gauge enabled the vacuum to be read. When the sand had been under vacuum for a given period, it was thoroughly mixed and a sample removed; water was once more poured on and the vacuum was maintained for a longer period. The results are given in Table III:

TABLE III.

Mesh screen.	Moisture at the end of			Vacuum In. mercury.
	5 min.	15 min.	30 min.	
30	7.20	5.69	4.75	1.5
40	8.20	6.84	5.19	1.75
50	8.65	7.50	6.41	0.75
60	8.42	7.38	6.90	2.0
80	9.15	7.52	7.37	2.25

It is seen from these results that the moisture content increases inversely as the diameter of the grains of sand. In each experiment the water pump was worked at full capacity, and as might be predicted, the vacuum increases slightly as the size of the grains decreases.

By way of comparison, a single experiment with sand of mesh 50 may be quoted. Water was poured on the layer and no vacuum was used; after 15 minutes' standing, the moisture content was found to be 27.4 per cent against the 7.50 per cent under vacuum.

The amount of liquid retained by different portions of a mass of grains in a filter, becomes important when the question of washing away an impure mother liquor has to be considered. A series of experiments was performed with the object of ascertaining the amount of water retained in the sands at different levels while under vacuum.

To carry this out, a tube about 80 cm. long and provided with side tubes closed with corks at 10 cm. intervals, was filled with each sand, and connected as has been described in the case of the Buchner funnel. A powerful water pump was run to full capacity and the pressure, as before, varied with the size of the

grain. The results are given in Tables IV and V:

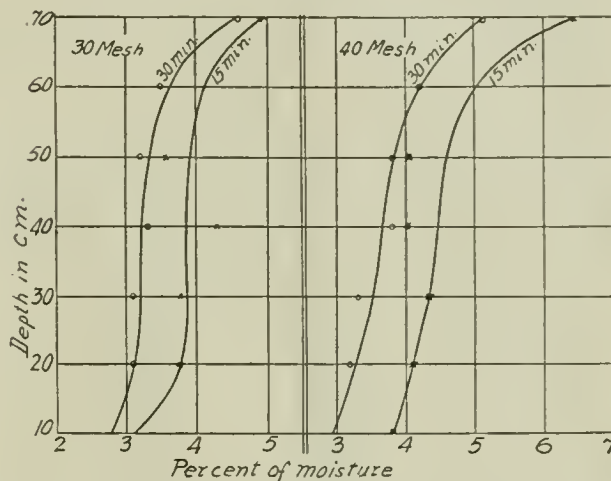
TABLE IV—PERCENTAGE MOISTURE AT END OF 15 MINUTES.

Mesh screen.	Pressure in. mercury.	Depth of sample from top in cm.							Mean per cent moisture.
		10.	20.	30.	40.	50.	60.	70.	
30	4.5	3.13	3.78	3.77	4.28	3.56	4.13	4.90	3.97
40	4.0	3.82	4.10	4.33	4.08	4.08	5.08	6.45	4.60
50	6.5	3.90	4.40	5.00	4.80	5.30	5.60	7.60	5.30
60	7.0	4.14	4.95	5.32	5.20	5.20	5.63	6.60	5.30

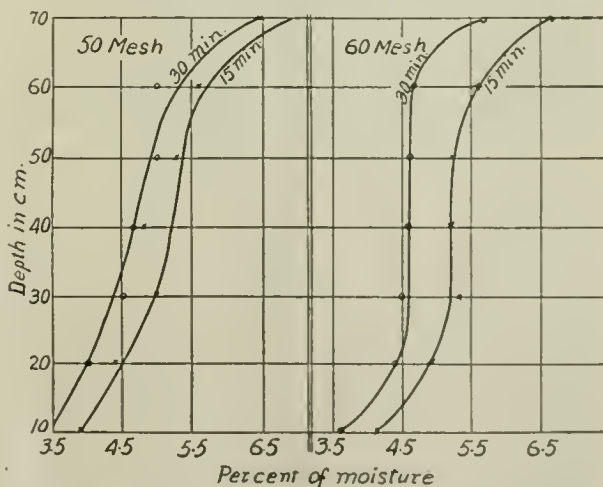
TABLE V—PERCENTAGE MOISTURE AT END OF 30 MINUTES.

Mesh screen.	Pressure in. mercury.	10.	20.	30.	40.	50.	60.	70.	Mean per cent moisture.
30	4.5	2.84	3.08	3.10	3.31	3.19	3.51	4.56	3.35
40	5.0	3.03	3.24	3.30	3.76	3.83	4.20	5.13	3.85
50	6.5	3.40	4.00	4.50	4.65	4.95	5.00	6.50	4.70
60	7.0	3.58	4.37	4.56	4.60	4.60	4.65	5.75	4.70

These results were plotted and curves were drawn as shown in the accompanying illustrations. The



individual points were sometimes decidedly off the curves, but although the experiments were repeated in these cases, no better agreement could be obtained; the accurate determination of small amounts of moisture in these sands proved to be difficult, probably owing to sampling. The average per cent of moisture



was determined by measuring the areas under the curve, and dividing this by the height which gave the width of the rectangle of equal area.

FILTRATION WITH CENTRIFUGE.

This well-known method of separating solids from liquids was next subjected to test for the sake of comparison with the previous experiments.

A small hand centrifugal, $4\frac{1}{4}$ ins. inside diameter, was used; it could be run at 5000 r. p. m. without any trouble. A cylinder of wire gauze, $1\frac{3}{4}$ ins. in diameter, was placed over the axis of the machine and the sand was poured into the annular space thus formed; the layer had, therefore, a thickness of $1\frac{1}{4}$ ins. which was the same as that in the Buchner funnel.

As a preliminary experiment, the sand was thoroughly wetted, and the centrifugal run at 2000 r. p. m. for 2 minutes. The percentages of moisture are given in Table VI:

TABLE VI—PERCENTAGE OF MOISTURE.		
Mesh screen.	Vacuum 15 min.	Centrifugal 2 min.
50	7.50	2.56
60	7.38	2.55

The marked efficiency of the centrifugal is noteworthy and the method of procedure was altered to show this more forcibly.

Sand was placed in the Buchner funnel, wetted and vacuum applied for 5 minutes. After sampling, the sand was placed while still moist, in the centrifugal which was then run for 2 minutes at 2000 r. p. m. Table VII shows the percentages of moisture:

TABLE VII—PERCENTAGE OF MOISTURE.		
Mesh screen.	Vacuum 5 min.	Centrifugal 2 min.
30	{ 7.25	2.26
	{ 7.12	2.20
40	{ 7.50	1.93
	{ 7.60	2.30
50	{ 8.70	2.56
	{ 8.60	2.80
60	{ 9.35	2.36
	{ 8.40	2.65
80	{ 9.70	2.49
	{ 9.56	2.46

It is seen from the above results, that the moisture content under vacuum varies inversely as the diameter of the grains; the moisture content after centrifuging, however, is nearly the same for the finer as it is for the coarser sands.

The distribution of the water at several points in the annulus of sand was also investigated and Table VIII presents the results in percentage of moisture.

TABLE VIII—PERCENTAGE OF MOISTURE.			
Distance from center of basket.			
Mesh screen.	$\frac{1}{2}$ "	1"	$1\frac{1}{2}$ "
40	2.9	2.72	2.43
50	3.0	2.90	2.76

The variation, while sufficient to permit measurement, is small and might be neglected for practical purposes.

The objection may be raised that these results, obtained in the laboratory with a small centrifugal, are of little value for comparison with the larger machines used in the factory. While with the hand centrifugal, the diameter is small, the speed is high, and we have calculated that a weight of 1 lb. revolving at a 2-in. radius at 2000 r. p. m. is subjected to practically the same centrifugal force as a weight of 1 lb. revolving at a radius of 12 ins. at 600 r. p. m. The comparison is, therefore, justifiable and a good idea of the behavior of a moist mass when centrifugal in

the factory, may be obtained beforehand in the laboratory.

Using the formula given by Griscom,⁵ we have calculated the pressure as the periphery of the $4\frac{1}{4}$ -in. centrifugal running at 2000 r. p. m. and find it to be 7.66 lbs. per sq. in.

THEORETICAL CONSIDERATION.

Hatschek⁶ has discussed the behavior of very finely divided substances on the filter, and has pointed out the value of a microscopic examination in this connection. The probable arrangement of the particles, with respect to the pores of the septum, are pointed out, and the influence of the flexibility of the latter is taken into consideration.

The retention of small quantities of liquid in the mass of fine grains is due, undoubtedly, to capillarity. The extraordinary difficulty in removing the last few per cent is well known and is again set forth above. In considering the reasons for this, it seemed to be worth while to calculate what would be the thickness of the film, if all the residual water were assumed to be distributed uniformly over the superficies of the grains. For this purpose, sand of 30-mesh with 6 per cent moisture was selected; the thickness of the film of water on each grain was found to be 0.0116 mm.

It would be interesting to calculate what stress must be applied to a grain thus coated, to overcome the surface tension of the liquid in so far as to allow the removal of at least part of the water; such a computation, if it could be effected, might furnish a scientific basis for the prediction of the behavior of finely divided solids on centrifuging. The authors have been unable to find time to carry this out, but hope to do so in the future.

The above discussion assumes that all the water is present on the superficies of the grains, but the capillary action of the small spaces between the grains is undoubtedly of great importance. In the case of the sand just quoted, which has a pore space of 35.4 per cent, the moisture present would fill 30 per cent of this; that is, 70 per cent of the pore space is filled only with air. This gives some idea of the comparatively poor performance of the ordinary filter and of the vacuum filter; in each case, air channels form and the downward pressure on the water-filled pores is thus relieved. In the case of the centrifugal, each particle of water experiences practically the same stress, and only the capillarity of the finest pores and the surface tension of the films on the grains are sufficient to resist its action.

SUMMARY.

1—The pore space in a mass of fine grains averages about 37 per cent of the total volume.

2—The amount of water retained when an ordinary filter is used varies from 11 per cent, with 20 mesh material, to 20 per cent with 100 mesh material, one hour being allowed for drainage.

⁵Metal. and Chem. Eng., April, 1913.
⁶Loc. cit.

3—The amount of water retained on a filter with 2 in. vacuum averages 7 per cent after 15 minutes for material varying from 30 to 80 mesh.

4—In a layer of material 7.0 cm. deep on a filter, with 5 in. vacuum, the top layer will average, after 15 minutes, 4 per cent moisture, and the bottom 6.5 per cent; the size of the grains is not of importance within the limits discussed. If the vacuum be maintained for 15 minutes longer, the above figures will be reduced by another half per cent.

5—By the use of a centrifugal, the percentage of moisture, in all the materials employed, may be reduced to an average of 2.5 per cent.

6—In the case of a sand of 30 mesh with 6 per cent moisture, if all the water be distributed over the surface of the particles, each grain would have a film 0.0116 mm. thick; or the water would fill 30 per cent of the pore space.

A METHOD FOR THE ESTIMATION OF PODOPHYLLUM RESIN.*

By W. M. JENKINS.

It seems to be a generally acknowledged fact that the therapeutic activity of Podophyllum is due to the resin which it contains. While this resin is recognized in the United States Pharmacopoeia, and its properties and solubilities are well described, it must be remembered that the resin is not a simple substance, but a mixture of substances, the most important of which is a crystalline body called Podophyllotoxin. From a therapeutic standpoint, however, Podophyllum Resin U. S. P., is a well known substance and the dose is well defined. It would seem therefore that any attempts at assaying or standardizing the drug should be in terms of Podophyllum Resin, U. S. P. It was with this idea in view that the work described in this paper was undertaken.

All previous methods for the determination of Podophyllum Resin have been based on the idea that the resin is insoluble in water, and that by pouring an alcoholic solution of the resin into a large volume of acidulated water the resin¹ would be completely precipitated and could be collected and weighed. Through long experience with this precipitation method, however, it has been found that the results are very unreliable and greatly affected by the conditions of the method, viz., the volume and temperature of the acidulated water, the amount of alcohol used and the amount of sample taken. The only way to get results which were at all concordant was to adhere strictly to the same amounts of alcohol, water, acid and sample; the results were thus purely arbitrary.

The reason for these variable results was later found to be the fact that Podophyllum Resin is slightly soluble in water and that this solubility is increased by small percentages of alcohol, and hence the recovery

of the full amount of resin by the precipitation method is impossible. Thus it was found that by dissolving 0.4 gram of U. S. P. Podophyllum Resin in 10 cc. of alcohol and precipitating the resin in 600 cc. of water acidulated with 10 cc. of hydrochloric acid, only 75 per cent of the resin was recovered.

Podophyllum Resin is only partly soluble in chloroform but is readily soluble in a mixture of 1 part of alcohol and 2 parts of chloroform. Hence it was thought that a mixture of alcohol and chloroform might be used for extracting the resin quantitatively from an alcohol solution which had been diluted with water.

When equal volumes of alcohol, chloroform and water are mixed, this mixture separates, on standing, into two layers. The upper portion consisting approximately of one part of alcohol and two parts of water, and the lower layer of one part of alcohol and two parts of chloroform.

By keeping the proportions of alcohol, chloroform and water constant, it was found that over 99 per cent of resin was recovered by three extractions with the alcohol chloroform mixture when working with U. S. P. Podophyllum Resin.

When this method was applied to the fluidextract, however, and the resulting resin compared with the U. S. P. Podophyllum Resin, it was found to be darker, more hygroscopic, less soluble in alcohol and more soluble in water. Thus it was necessary to modify the method in some way in order to obtain a resin identical with the official resin. This was accomplished by washing the alcohol chloroform extract with acidulated water. The resin obtained by this modification was found to conform to the United States Pharmacopoeia requirements for Podophyllum Resin, viz:

Soluble in alcohol in all proportions.
86.4 per cent soluble in ether.
69.1 per cent soluble in chloroform.
21.3 per cent soluble in boiling water.
0.1 per cent ash.

By this procedure from 0.4 gram Podophyllum Resin U. S. P. dissolved in alcohol, 0.394 gram was recovered, corresponding to 98.4 per cent.

Accordingly the following method for estimating the amount of Podophyllum Resin in Fluidextract Podophyllum is suggested.

Measure 5 cc. of Fluidextract Podophyllum into a separatory funnel, add 5 cc. of alcohol, 10 cc. of chloroform and 10 cc. of acidulated water containing 0.6 per cent hydrochloric acid (2 cc. HCl in 100 cc. water). Shake and allow the mixture to separate. Draw off the lower layer into another separatory funnel; repeat the extraction twice, using 15 cc. of a mixture of one part of alcohol and two parts of chloroform, each time, and add these extractions to the first. Shake the combined extractions with 10 cc. of the acidulated water and allow the mixture to separate. Draw off the lower layer into a tared flask, and repeat the extraction twice, using 15 cc. of the alcohol chloro-

*From the Journal of Industrial and Engineering Chemistry.

¹J. Chem. Soc. (Trans.), 1893, p. 209.

form mixture each time. Evaporate the combined extractions and dry the residue to constant weight at 100° C.

For comparison a number of fluidextracts were assayed by this method, and by the usual precipitation method with the following results:

RESIN IN FLUIDEXTRACTS.				
Precipitation method.		Shake-out method.		
G. in 10 cc.	Per cent.	G. in 5 cc.	Per cent.	
1.....	0.424	4.2	0.3480	6.9
2.....	0.420	4.2	0.3130	6.2
3.....	0.420	4.2	0.2895	5.7
4.....	0.458	4.5	0.3430	6.8

In assaying the drug, 10 grams in a No. 60 powder are placed in an Erlenmeyer flask, and 25 cc. of alcohol are added. The flask is then fitted with a stopper through which is inserted a glass tube about two feet long for a condenser and left on a sand bath at 80 C. for three hours.

The contents of the flask are then transferred to a small percolator and washed with alcohol until about 50 cc. of percolate are obtained. When cooled to room temperature, the solution is made up to exactly 50 cc. Of this solution, 10 cc., representing 2 grams of the drug, are used for assay, which is carried out in exactly the same way as described for the fluidextract, with the exception of the addition of the 5 cc. of alcohol, which is omitted.

It was found that it required at least 48 hours maceration with cold alcohol to exhaust the drug, and hence the hot maceration is advisable.

Six different samples of Podophyllum were assayed by this method, and from the same samples fluidextracts were made according to the directions in the United States Pharmacopoeia, and were also assayed. The results are given below:

	Grams resin in 100 grams drug.	Grams resin in 100 cc. fluidextract.
1.....	5.03	4.96
2.....	5.24	5.16
3.....	4.65	4.66
4.....	4.92	4.89
5.....	4.73	4.83
6.....	6.82	6.71

These results show that the method gives very concordant results on the assay of the drug and fluidextract and much higher results than the precipitation method. If the method gives equally good results in the hands of other workers, then it would be advisable that fluidextract of Podophyllum, U. S. P., be assayed and standardized. As good lots of Podophyllum drug contain 5 per cent of resin, a standard of 5 per cent resin for the fluidextract is suggested.

The method can also be applied to the assay of solid and powdered extracts of Podophyllum by dissolving weighed quantities of the extracts in sufficient alcohol to render the solutions of about the same strength as fluidextract.

In 1912 the United States produced 37,478 short tons of barytes, valued at \$153,313, or \$4.09 a ton, and imported 26,186 short tons of crude barytes, valued at \$52,467. In 1913 the domestic production was 45,298 short tons.

A NEW SYSTEM OF TREATING PHOSPHATE ROCK.

The larger brown rock operators in Tennessee have for some time been using the most improved machinery for removing overburden, and for washing and drying the phosphate; but the most distinct advance yet made will be inaugurated when one of the large Tennessee concerns starts its first new preparation plant about September 1st. The engineering experiments for this were begun in March, 1913. When the principle was worked out, a model was built. Four months were given to experimentation with this until the practicability of the principle was thoroughly demonstrated. Then the work on the first new plant was started. Every feature of the former system of preparation in the Tennessee field has been abandoned in the new system, states the *American Fertilizer*.

The process has not been made public, but it is known that one feature involves the principle of gold ore preparation, that of wet stamping, which reduces about eighty per cent of the phosphate rock to a degree of fineness which requires no further reduction for acidulation. It is claimed for the new product that even rock carrying the smallest percentage of phosphate of lime will contain no more of the oxides of iron and alumina than the guarantee for several years has been on Tennessee rock of export grade; that the "available" will be largely increased in acid phosphate made by the new method, because of the decreased quantity of sulphuric acid required for dissolving the rock; and that the acid phosphate will dry down to 12 per cent within a comparatively short time of curing, leaving only a minimum of insoluble and no trace of free acid. The new product will be sold upon wholly new guarantees and allowances for deficiencies of phosphate of lime or excesses of the oxides, and is expected to establish a higher standard of acid phosphate, both in percentage of available and mechanical condition, than has ever in quantity been put upon the American market.

A serious phase of the interruption to commerce caused by the European war is the shutting off of the foreign supply of ferromanganese from the steel manufacturers of this country. The United States Geological Survey states that the domestic marketed production of ferromanganese and spiegeleisen in 1912 and 1913 was 227,939 long tons and 226,475 long tons, respectively, while the imports of these alloys for those years were 100,152 long tons and 128,147 long tons, respectively, of which ferromanganese constituted 99,137 long tons in 1912 and 128,070 long tons in 1913. The imports of these alloys therefore constituted 30.5 per cent and 36 per cent, respectively, of the available supply in 1912 and 1913. England and Germany have furnished most of these imported alloys in recent years. By far the greater part of the ferromanganese produced in the United States is manufactured by steel companies for their own consumption.

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NOTES AND COMMENTS.

Effect of War on Supply of Potash Salts.

Outside of Germany there is no known commercial supply of potash salts. If the German supplies are cut off during the European war, the agricultural world must either go without potash salts after the meager supply now on hand is exhausted or bestir itself to find another adequate source of supply. Already many inquiries regarding potash have been addressed to the United States Geological Survey, and the fertilizer journals report that small quantities of spot material are changing hands at sharp premiums. The situation is undoubtedly more acute than it was a few years ago, when national interest was first awakened to the fact that the United States is entirely dependent on Germany for this important class of fertilizer materials.

Potash salts are employed in many industries other than the fertilizer industry. A large amount is used in glass and soap making and in the manufacture of a number of chemical products. These include potassium hydrate, or caustic potash, and the carbonate and bicarbonate of potash, used principally in glass and soap making; the potash alums; cyanides, including potassium cyanide, potassium ferro-cyanide, and potassium ferri-cyanide; various potash bleaching chemicals, dye stuffs, explosives containing potash nitrate, and a long list of general chemicals.

The needs of the manufacturers and the farmers of the country are well known and keenly appreciated by the Geological Survey. Since the question of a domestic supply of potash salts has become of public interest, the Government has endeavored to locate deposits in this country, and has followed up every clue that seemed to promise results of importance. The Survey's work has extended from New York to Cali-

fornia and from Michigan to Louisiana, and has covered all branches of investigation where results might be expected, exclusive of the study of kelp. Its investigations have been carried out along several lines. (1) Deep drilling for saline residues has been done at Fallon and, during the past year, in Columbus Marsh and Black Rock Desert, Nevada, and will be continued in Black Rock Desert this year. (2) Natural and artificial brines and bitterns have been collected at all the salt-making establishments in the United States and a great many other localities, and examined. (3) Deposits of alunite and other minerals, containing potassium, have been investigated in Utah and other states. (4) Certain occurrences of igneous rock known to contain considerable quantities of potash salts have been examined. Much work has also been done by private initiative along practically all the lines mentioned above. The Bureau of Soils, of the Department of Agriculture, has investigated the kelps. The work is not yet finished and will be pushed with increased vigor, provided the necessary funds are supplied.

The imports of potash salts, listed as such in the reports of the Bureau of Foreign and Domestic Commerce, include the carbonate, cyanide, chloride, nitrate and sulphate, caustic potash, and other potash compounds. The importation of the above salts in round numbers the last three years has averaged 635,000,000 pounds in quantity and \$11,000,000 in value. These figures, however, represent only a part of the potash salts entering the United States, as they do not include the imports of kainite and manure salts which are used in fertilizers. The quantity of this class of materials imported for consumption in the United States during the last three years has averaged about 700,000 tons, valued at \$4,300,000, annually. Thus it is apparent that the annual importations of potash salts exceed \$15,000,000.

A New Manure.

According to the *American Fertilizer*, a process is now being tried in Sweden for the preparation of potassic fertilizers from potash-bearing rocks. A rock of a similar chemical composition to feldspar, containing up to 11 per cent potash, is mixed with coal and iron filings and treated in an electric oven. The silica in the rock is partly reduced and combined with iron to form silicon iron, and leaves the potash combined with silica, but in a more soluble form than the original raw material. This slag, when cold and finely ground, forms a gray powder, and is sold under the name of electro-potash (electrokali). Some of the experiments carried out with this elektrokali gave yields equal to 78 per cent of the crops obtained from sulphate of potash. The solubility of the slag was increased by changes in the method during last year, and it does not seem improbable that further trials will yield a still more soluble potash.

RECENT PATENTS.

The following patents relating to industrial and engineering chemistry are reported by C. L. Parker, McGill Bldg., Washington, D. C.:

1,102,330. Finish-Remover. Carleton Ellis, Larchmont, N. Y. Patented July 7, 1914.

1,102,339. Process for Treatment of Minerals and Extracting Metal. Buenaventura Junquera, Oviedo, Spain. Patented July 7, 1914.

1,102,358. Process of Making Magnesium Cement. William Siegmann, Baltimore, Md. Patented July 7, 1914.

1,102,473. Acid Proof Packing Material. Marvin Lee Chappell, Berkeley, Cal. Patented July 7, 1914.

1,102,670. Process of Producing Sulfuric-Acid Anhydrid According to the Contact Process. Herman Von Keler and Anton Weidel, Leverkusen, Germany. Patented July 7, 1914.

1,102,827. Process of Producing Sulfonic Acids. August Vagt, Leverkusen, near Cologne, Germany. Patented July 7, 1914.

1,103,017. Oxidation Process. Carleton Ellis, Montclair, N. J. Patented July 7, 1914.

1,103,081. Process of Recovering Sulphur in Elementary Form From Pyrite. Gilbert Rigg, Palmerston, Pa. Patented July 14, 1914.

1,103,092. Compound for Extinguishing Fires. Walter O. Snelling, Pittsburgh, Pa. Patented July 14, 1914.

1,103,115. Fertilizer and Process for Producing the Same. Frank S. Washburn, Nashville, Tenn. Patented July 14, 1914.

1,103,165. Process for Rendering Smelter Fumes Useful and Recovery of Their Values. Charles S. Vander, Salt Lake City, Utah. Patented July 14, 1914.

1,103,266. Varnish and Process of Making Same. Michael F. Coughlin, Stoughton, Mass. Patented July 14, 1914.

1,104,095. Process of Making Superior Sugar. Neils Breinholt Bach, Modjo, Java. Patented July 21, 1914.

1,104,105. Process of Making Substitutes for Animal Wool. Candido Chavez, Mexico, Mexico. Patented July 21, 1914.

1,104,107. Metal Pickling Process. Thomas Reginald Davidson, Westmount, Quebec, Canada. Patented July 21, 1914.

1,104,376. Soy Milk Product and Process of Making the Same. Louis J. Monahan and Charles J. Pope, Oshkosh, Wis. Patented July 21, 1914.

1,104,590. Manufacture of Sulfuric Acid. Utlely Wedge, Ardmore, Pa. Patented July 21, 1914.

1,104. Process of Making Bisulfite of Soda. Henry Howard, Boston, Mass. Patented July 28, 1914.

1,104,912. Method of Extracting Rosin from Resinous Wood. Frank E. Lichtenhaeler, Newton, Mass. Patented July 28, 1914.

1,104,913. Process for the Manufacture of Sodium Bisulfate in a Directly Calcinable Form. Peter Löffler, Vienna, Austria-Hungary. Patented July 28, 1914.

1,104,922. Process for the Extraction of Zinc from Zinc Bearing Refuse. Ralph R. Parish, Waterbury, Conn. Patented July 28, 1914.

1,105,060. Cork Article and Method of Making the Same. Herman F. Busch, Pittsburgh, Pa. Patented July 28, 1914.

1,105,119. Process of Removing the Bitter Taste from Malt Extracts. Rudolf Weyermann, Bamberg, Germany. Patented July 28, 1914.

1,105,304. Process of Making Calcium Acid Phosphate. Elliott W. Reed, Savannah, Ga. Patented July 28, 1914.

PRODUCTION OF PLANTATION RUBBER IN BURMA.

Hevea rubber was first introduced into Burma in 1877, when a small consignment of plants was sent from Kew Gardens to Mergui. A second consignment was obtained from Ceylon in 1879. This was the beginning of the Government experimental garden, the results obtained from which proved conclusively that Hevea rubber could be grown in Burma. In 1910 the Government sold the experimental garden to the Mergui Crown Rubber Estates. There is on this estate a 50-acre block of 35-year-old rubber trees. Girths of 70 to 80 in. are common, the largest tree measuring 108 in., and their average yield is 12 to 15 lbs. per tree.

The chief planting centers are Mergui with King Island 18 miles distant, and Victoria Point lying 220 miles south of Mergui, distant two days by steamer and forming the frontier between Burma and Siam. Weekly steamers ply between Rangoon and Mergui, taking two days for the trip. Other important districts where rubber has been planted are in Amherst district, near Moulmein; at Twante, near Rangoon; at Hlawga, 15 miles from Rangoon; at Shwegyin, Toungoo district; and in the far north, close to the Chinese border, at Myitkyina.

According to U. S. Consul Maxwell K. Moorhead, the climate of the rubber-producing areas of Burma may be divided into four seasons, viz, the dry season, Dec. 1 to March 31, in which practically no rain falls; the rainy season, June 1 to Sept. 30, during which 90 per cent of the total precipitation of the year occurs, 62 to 147 in.; the preliminary rainy season, April 1 to May 31, when 9 to 24 in. fall; and the declining rainy season, Oct. 1 to Nov. 30, 9 to 12 ins. In the year from April 1, 1912, to March 31, 1913, there were 142 rainy days in the Mergui district, on which a total of 169.91 in. of rain fell; in Amherst, 143 days and a total of 182.63 in.; Rangoon, 126 days, precipitation 93.97 in.; Toungoo, 119 days, precipitation 85.12 in.; and Myitkyina, 113 days, precipitation 88.75 in.

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COAL AND THE CHEMISTRY OF ITS CARBONIZATION.*

By JOHN HARGER.

Very little is known of the chemical composition of the various constituents of coals, though some progress has been made in separating them by the solvent action of pyridine, discovered by Professor Bedson. Coals, such as anthracite, semi-anthracite and steam coals, yield very little pyridine-soluble matter, neither do brown coals nor cannals yield very much, but some bituminous coals give as much as 40 per cent extract. The utility of the pyridine extraction method is, however, impaired by the facts that the ultimate chemical analysis of the soluble and insoluble portions from the same bituminous coal differ very little, and that, up to now, all the fractions contain more nitrogen than the original coal, indicating that some pyridine, in spite of all precautions to remove it, is retained by the coal substances. By the usual Soxhlet method the quantity slowly dissolved by pyridine is large at first, then more is dissolved very slowly, an extraction usually extending over two weeks at least. The author has found that a better way is to take a small quantity of the finely powdered coal (passing through 120 mesh sieve), say, about 1 gramme, add 150 grammes of pyridine, seal in a strong glass tube and heat to about 160-180° C. for 24 hours. By this method more extract is obtained in 24 hours than by the usual method in months.

The chemists at the Government Experimental Station have found that the inflammability of coal dust is in proportion to the quantity soluble in pyridine. The French Government chemists, however, find that, for French coals at least, this relation does not apply. The author has found that canal coal contains very much less soluble in pyridine than ordinary bituminous coals, by the Soxhlet method. Old Roundwood canal yields 15½ per cent, and Lancashire Arley coal 22½ per cent, yet there is no doubt that the canal dust is far more inflammable than the dust of the Arley coal. It was found, however, that Arley coal dust, which gave only 22½ per cent soluble in pyridine by two weeks' extraction in the Soxhlet, gave 40½ per cent soluble in pyridine by the sealed-tube

method; 150 grammes of a different sample of Arley coal, but taken from the same mine, was extracted first by chloroform and then by several portions of pyridine, boiling up in each case for a long time until only a trace of soluble matter was obtained. A portion of the residue was then taken and heated in a sealed tube for 34 hours at 160-180° C., and the residue from this heated with a fresh portion of pyridine for 24 hours at 160-180° C., with the following results, stated on the dry and ash-free substance.

Some of these fractions were saturated with chlorine, after removal of pyridine, etc., in a current of inert gas at 150° C., and the increase in weight is stated below. Chlorine and hydrochloric acid were removed *in vacuo* over sodium hydroxide. Increase in weight, per cent, Fraction B, 74.4; C, 64.4; E, 55.7; F, 31; H, 64.2. A considerable number of experiments have been made on the action of chlorine at high temperatures. CH₃Cl, CH₂Cl₂, CHCl₃, CCl₄ and C₂Cl₆ in considerable quantities were obtained.

The fact that pyridine dissolves the so-called resin bodies so very slowly and dissolves much more with the slight increase in temperature by the sealed-tube method, shows that this is not a case of ordinary solution. The extract once obtained is quite readily soluble in pyridine and gives a thick, viscid, tar-like mass, and that it is not "absorbed" by the insoluble portion of coal is shown by examination of thin sections which show the resinous bands and nodules to be separate from the general matrix. There appears to be some kind of simplification in the constitution of the constituents which yield the pyridine soluble matter, a process similar to depolymerization and due to the action of pyridine and heat. This is similar to the behavior of many ordinary resins which are only soluble in certain solvents after they have been heated at moderately high temperatures for some time. Clark and Wheeler have shown that the pyridine extract from Silkstone coal can be separated into two fractions by the solvent action of chloroform, and the author has found that this is the case with the pyridine extract from Arley coal also. The solution by chloroform is an extremely slow process and requires about two weeks to make the extraction complete. This points to either absorption or depolymerization. An interesting point is that this chloroform-soluble portion does not appear to be in the original coal as

*Abstract by the American Gaslight Journal of a paper read before the Liverpool Society of Chemical Industry.

such. There is some portion of Arley coal soluble in chloroform and the quantity seems to vary very much with coal even from the same seam. In one experiment it was as much as 3.9 per cent, but generally it did not exceed $1\frac{1}{2}$ per cent. This substance contained no sulphur and no nitrogen and gave on analysis: Hydrogen, 8.81 per cent; carbon, 83.92; oxygen, 7.27. The portion dissolved out of the pyridine extract by chloroform was rather more than one-third of the total pyridine extract, and this material contained nitrogen and sulphur as well as carbon, hydrogen and oxygen.

In the paper by Clark and Wheeler, results of extraction of Silkstone coal by pyridine, and subsequent action of chloroform on the extract obtained, are given with analysis of the various fractions. From their figures it is evident that all fractions contain more nitrogen than the original coal, and it appears on calculation that pyridine amounting to 4 per cent on the coal taken has been retained by the fractions. Examination of their figures also shows that in the extraction by pyridine and subsequently by chloroform a considerable quantity of oxygen has been absorbed and some sulphur lost. The figures show that: (1) 100 parts of coal have retained slightly more than 4 per cent of pyridine. (2) Oxidation has occurred in both extractions, but especially with chloroform, where the oxygen has increased by nearly 60 per cent. (3) There is a loss in sulphur in both extractions.

It might be gathered from these figures that the absorption of oxygen is an essential feature in the solution of these constituents by pyridine and chloro-

form, but the fact that more is dissolved by treatment in a sealed tube in absence of air proves that this is not so. The fact that pyridine is retained by the fractions even after heating *in vacuo* at 100°C . for several days has been proved by heating a portion of pyridine extract in a current of nitrogen at 150°C . The gas which came off contained pyridine, and was passed through H_2SO_4 which is distilled later with potash and the distillate titrated. This experiment showed the presence of 3.7 per cent of pyridine in the material. Later experiments have shown that the portion insoluble in pyridine contained pyridine after heating *in vacuo* for several days at 100°C ., and it has been found much more difficult to remove all the pyridine from the insoluble than from the soluble fractions.

The Coking Problem.—Not every coal gives a satisfactory coke on carbonization. A coal which will coke must contain a certain minimum quantity of bituminous matter. The coals selected for making metallurgical coke contain sufficient bituminous matter to fuse on heating to a few degrees above 310°C . The mass of washed coal is converted on heating to a pasty mass, from which, on further heating, the volatile matters distil, leaving a fixed carbonaceous residue which becomes harder and stronger the higher the temperature employed, because volatile hydrocarbons are decomposed, with deposition of carbon, in proportion to the temperature of the solid material through which these volatile hydrocarbons have to pass. With very high temperatures the product is hard and will withstand considerable pressure.

It appears that the coking properties of coals must

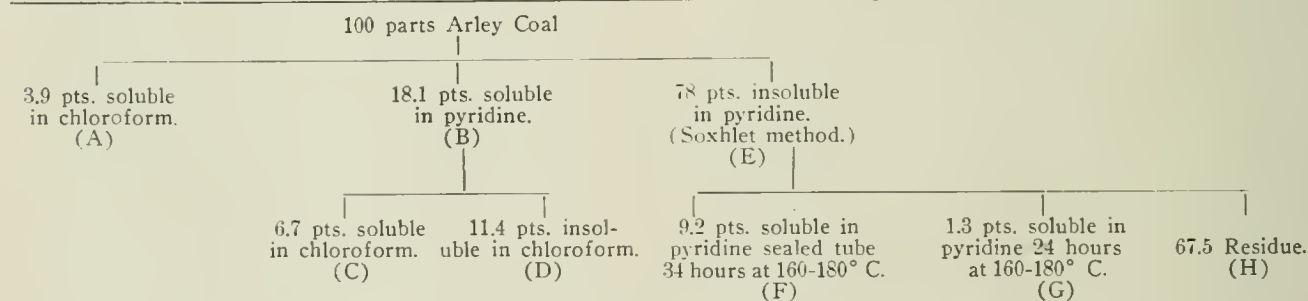


TABLE I.—SHOWING CHANGES DURING THE SEPARATION OF SILKSTONE COAL FRACTIONS, BY CLARK AND WHEELER.

		A.	B.	C.	D.		E.	F.		
		Original	Insoluble in	Soluble in	Average of 80 pts. B, 20 pts. C, (should equal A).	Diff. + or -	Insoluble in CHCl_3 .	Insoluble in CHCl_3 .	Average of 12 pts. of E, 8 pts. of F, (should equal C).	Diff. + or -
All Calculated on Ash and Moisture-Free Coals.		100 pts. Coal.	80 pts. Pyridine.	20 pts. Pyridine.			12 pts. in CHCl_3 .	8 pts. in CHCl_3 .		
Proximate Analysis.....	Volatile matter	36.79	34.96	55.24	39.02	2.29	31.88	77.33	50.06	5.18
	Fixed carbon	63.27	65.04	44.76	60.98	2.29	68.12	22.67	49.94	5.18
Ultimate Analysis.....	Carbon	82.92	80.81	82.89	81.26	1.66	77.32	85.33	80.52	2.37
	Hydrogen	5.58	5.23	7.14	5.61	0.03	5.14	7.08	5.91	1.23
	Oxygen	8.45	10.40	6.62	9.64	1.19	14.26	4.56	10.38	3.76
	Nitrogen	1.31	2.14	1.91	2.09	0.74	2.07	1.71	1.92	0.01
	Sulphur	1.70	1.42	1.44	1.42	0.28	1.21	1.32	1.25	0.19

be due to some compounds of C, H, O, N and S, about which little further is known than that they melt at about 320° C. Anderson and Roberts showed that coals of the Clyde Basin began to soften at 310° C. and melted fairly completely at 320° C. The best coking coals melted at 317° C. The older coals coked, the newer ones did not.

	Carbon.	Hydrogen.	Oxygen. Etc.	Coking Power.
Non-coking	82.65	5.55	10.1	3.9
Semi-coking	83.16	5.48	8.98	4.4
Coking	85.41	5.36	7.22	13.5

It is not possible to tell from the ultimate analysis of a coal whether it will coke, but it is often found possible to say that it will *not* coke. Cases are known of coals of exactly the same ultimate chemical composition some of which coked quite well and the others not at all. An essential part of the process of coking takes place between 250° C. and 400° C. If coking coal is carbonized below 400° C., then powdered and heated to very high temperatures such as are employed in metallurgical coke ovens, there is no sign of sticking together of the particles. It is generally believed that it is the quantity of the so-called resinous constituents in coal which determines its coking or non-coking property. According to Anderson, this has been proved to be wrong, but on what evidence is not clear. A study of his papers reveals no facts supporting his conclusion.

Some of the fundamental facts about the coking property are: (1) The coking property in some coals is destroyed by exposure to air, and even in more strongly coking coals it is sensibly diminished. (2) The coking property in some coals is destroyed, in others weakened and in some not affected by boiling with dilute caustic potash. (3) Heating in a current of inert gas at 300° C. for several hours destroys the coking power of some coals and weakens it in all coking coals; but the strongly coking coals retain sufficient to coke when strongly heated.

Anderson and Roberts conclude, and Professor V. B. Lewes agrees, that strongly coking coals, in addition to the so-called resin bodies, contain substances which are not soluble in alkali, do not oxidize in warm air, and do not decompose or volatilize at 300° C.; and that substances of this class melt on strongly heating and yield enough luting material to form coke. They call these substances "hydrocarbon bodies." The assumption of the existence in coal of a class of compounds called hydrocarbons, on such evidence, is not, in the author's view, justifiable and they must be omitted from the constituents of coals. (Hydrocarbons have been found only in mere traces in coals.)

The phenomena described above would be observed if the so-called resin and other bodies on slow heating, etc., decomposed and yielded, amongst other products, a *smaller* quantity of substance which was fusible at higher temperature, and this is what the author has found does actually take place. The true coking coals contain sufficient resin-like bodies to yield, after heat-

ing at about 300° C., sufficient fusible material to form coke when heated to 320° C. or above. While the feebly coking coals on heating, etc., gave the same kind and proportion of fusible bodies, the quantity was not sufficient to melt or render liquid the whole of the material and so coke could not be formed.

A sample of Arley coal extracted with chloroform gave 1.2 per cent soluble: on heating another portion of the coal to 230° C. in inert gas for 5 hours it gave on extraction 1.4 per cent soluble in chloroform. A third portion, heated for 5 hours at 270° C., gave on extraction 7.6 per cent soluble in chloroform. A fourth portion was alternately heated to 330-340° C. in inert gas, and extracted with chloroform five times; the total time of heating was 22 hours, and the total of the chloroform extracts amounted to 8½ per cent of the original coal. It is evident that a subtle change starts in Arley coal at about 250° C., and at 270° C. it is very marked, although the coal is changed very slightly in appearance and no permanent gas appears to be evolved. Experiments were made to ascertain which part of the coal gave rise to these products soluble in chloroform. Pyridine extract after heating to 340° C. gave 8.2 per cent, and pyridine residue after similar treatment gave 1.6 per cent. It is therefore evident that both constituents give rise to the products.

Nitrogen in Coal.—There is evidence to show that nitrogen occurs in coal combined in two or more essentially different ways. A small quantity of the total is given off as ammonia on carbonization, while half of it remains in the coke, indicating that it occurs in coal combined in at least two ways and probably more. It has been observed that in some coals the nitrogen estimated by the Kjeldahl method is a mere trace, when a Dumas estimation reveals there is about 2 per cent. In other coals the two methods give exactly the same amount, showing that the nitrogen is not held the same way in all coals. It has been further observed that when some coals are mixed with caustic soda and ignited, much less nitrogen remains fixed in the residue of the untreated coal, and it has been observed that other coals, when treated in a similar way with caustic soda, etc., had more of their nitrogen fixed than when heated alone. Some of the fixed nitrogen can be converted into ammonia by passing hydrogen over the red-hot coke, but the only practical method hitherto devised of increasing the yield of ammonia is to burn the coke while keeping the temperature as low as possible, as in the Mond producers. The nitrogen which comes off as ammonia on the carbonization of coal probably exists in side-chain groups, while that which remains fixed in the coke probably occurs in ring compounds, the ring being stable at a red heat.

Over twenty years ago R. J. Friswell discovered that by acting on powdered coal with nitric acid of about 50 per cent strength, a complex organic acid or acids were obtained, which decomposed sodium car-

bonate with evolution of carbon dioxide. These bodies, which were later called the coal acids by Anderson, are insoluble in water containing much mineral acid, but in pure water or dilute alkali or dilute acid they are soluble, giving an ink-like solution. The solid coal acids on heating with zinc dust gave hydrogen, cyanogen, and a small quantity of aqueous distillate, smelling of ammonia and pyridine, and containing hydrocyanic acid. Anderson worked on compounds made from very different kinds of coals by treating with nitric acid, and found that the resulting coal acids had about the same ultimate chemical composition. It seemed probable that the nitric acid oxidized all the side-chains, giving COOH groups attached to a nitrogen ring complex. To test this the author oxidized some Arley coal with fuming sulphuric acid (so as to keep nitrogen containing reagents out of the experiments) and obtained similar compounds to those got by Friswell and by Anderson. The solid purified coal acid was mixed with caustic soda and heated. A gas smelling like charred albumen or bone was obtained, and the same was obtained several times on repeating the experiment with fresh quantities of coal. This would appear to indicate that coal contains nitrogen in the form of a ring complex, which on oxidation with fuming sulphuric acid is converted into a carboxylic acridine.

The author then referred to the Coalite process, in which the coal is carbonized at about 650° C., giving a coke not so friable. The yield of sulphate is raised from 12 pounds to 28 pounds; the tar reduced to 18 gallons, and the gas increased to 8,500 cubic feet per ton of an average bituminous coal. He also referred to the low-temperature carbonization *in vacuo*, and pointed out that as much as 80 to 100 gallons of coal oils were obtainable from some cannel coals by this process, a considerable portion of which could be converted into petrol (8 to 10 gallons) and a large proportion of the remainder into oils suitable for use in Diesel engines. Another low-temperature carbonized process, the "Del Monte," was briefly mentioned. None of these processes are intended to replace either gas works practice or metallurgical coke ovens, and the author questioned whether, in view of the demand for a smokeless fuel and the great advance in the value of petrol and oil, the modern gas works' practice of obtaining as much as possible per ton of coal had not been overdone, and if the old lower temperature of carbonization was not more suitable to present needs.

As regards metallurgical coke it was also a question whether this could not be produced in two stages, viz., (1) carbonization at a sufficiently low temperature to preserve the valuable light oils and give rich gas; and (2) high temperature carbonization to give the finished hard coke and poor gas.

Both the gas works manager and the coke-oven manager can learn that, under certain conditions, it was not a question of how difficult it was to heat up coal, but how difficult it was to prevent it heating up spon-

taneously; also that a gob-fire could give a beautiful hard coke with coal which no existing coke-oven could coke at all. Practically any bituminous coal could be coked in favorable circumstances, but ordinary coke-oven processes do not give these favorable conditions.

THE EXPLOSIBILITY OF GRAIN DUSTS.*

As a result of a number of explosions in grain mills and industrial plants in this country and in Europe, and more especially as a result of an explosion in a feed-grinding plant at Buffalo, New York, in June, 1913, by which thirty-three men lost their lives and upwards of seventy were injured, a co-operative movement between milling interests generally and the Bureau of Mines was arranged for the purpose of making a scientific study of the explosibility of grain dusts, and of methods pertaining to the prevention of such explosions. The milling interests were represented in the conduct of the work by Messrs. Lawrence E. Harmon, president of Buffalo Cereal Company; Frank F. Henry, manager, Washburn-Crosby Company; and George P. Urban, secretary, George Urban Milling Company, all of Buffalo, New York.

This work was started August 1, 1913, being placed under the direction of Prof. George A. Hulett, Chief Chemist of the Bureau of Mines. David J. Price was assigned to the field-engineering work, and on February 1, 1914, Dr. H. H. Brown began a laboratory study of the problem.

During the preliminary study thirteen explosions were investigated which have occurred since 1905. Three of these took place in Iowa, three in New York, two in Illinois, and one each in Vermont, Indiana, Kansas, Ohio and Texas. These explosions were classified among the various lines of milling as follows: Cereal mills, 4; elevators, 3; feed mills, 2; starch factories, 2; glucose factory, 1; flour mill, 1. It is reported that, as a result of these explosions, at least seventy-eight men were killed and 119 injured. The total damage to property exceeded \$2,000,000.

Since 1911 four explosions have occurred in Europe, two in dextrine works, one in a provender mill, grinding peas, beans, and wheat, and one in a linseed mill. As a result of these explosions forty-seven men were killed and 119 injured.

In order to make a laboratory study of the problem, samples of the following dusts were collected, and the conditions under which they were produced were studied:

1. Dusts produced during the process of elevating and handling grain, and known as elevator dusts;
2. Wheat-flour dusts from rolls, bolters, purifiers, conveyors, packing machines, etc.;
3. Wheat-flour dusts from beams, rafters, elevator heads, etc.;

*Abstract of a preliminary report by David J. Price and Harold H. Brown; published by the Millers' Committee of Buffalo, N. Y.

4. Dusts produced during the cleaning of oats;
5. Dust from grinding white corn;
6. Dust from grinding yellow corn;
7. Dust from grinding oat hulls;
8. Oatmeal dust from packing machines;
9. Floor dusts from elevator sweeping;
10. Oat-groat dusts after aspirator.

These dusts were first analyzed in the United States Food and Drug Laboratory, Chicago. Determinations of moisture, ether extract, proteins, crude fiber, ash and nitrogen-free extract or carbohydrates, were made to ascertain, not only the chemical nature of the materials, but also wherein they might differ from the grains from which they originated.

Experiments were then started in the Bureau of Mines, Pittsburgh, to determine the ignition-temperature of these dusts, using the method of Wheeler.¹ This consisted in forcing the dust in a cloud through a glass tube, three inches in diameter and fifty-five inches long, against a heated platinum coil, which was 15.75 inches from one end of the tube. The temperature of the coil was obtained by a Pt-PtRh thermocouple, having its hot junction within the quartz tube upon which the coil was wound. Using this method, Wheeler determined the ignition-temperature—temperature of propagation—of many dusts, obtaining results varying from 805° C. for sugar, 960°-1035° for starch, 990° for oat hucks, 995° for grain (flour-mill), to 1060° for flour and 1100° C. for castor-oil meal. The results obtained upon grain dusts by the author varied from 995° C. for oat and corn elevator dusts, 1015° for feed dust from dust collector, 1020° for ground oat hulls, 1025° for yellow-corn dust, to 1115° for wheat elevator dust and 1235°-1270° for flour dusts. Wheeler worked with samples which had been dried at 107° C., while the author used the samples as received from the mill.

While the work gave the relative ignition-temperatures it did not give the lowest temperature of ignition or the relative inflammability. This latter was determined by means of an apparatus developed in the Bureau of Mines. It consists of an explosion flash of about 1400-cc. (85-36 cubic inches) capacity having two tubulars, a platinum coil, a device for driving a dust cloud against the coil, and a Crosby pressure-gage for measuring the pressure developed. In each determination 50 mg. (.00176 oz.) of the dust is forced in a cloud against the coil, which has been previously heated to a known temperature determined by a thermocouple. The temperature is that inside the coil and therefore higher than the actual temperature on the outside of the coil. The dust is ignited by the heated coil and a pressure developed within the flask, which is registered by the gage. The relative inflammability at any temperature is measured by the difference in the pressures developed within the flask.

Determinations were made of pressures developed by the different dusts, as received and dried at 105° C., when they were forced against the coil heated to 1200°, 1100°, 1000° and 900° C. As no standard has been taken for carbonaceous dusts, other than coal dust, Pittsburgh standard coal dust, which is very constant in its properties, and which is used as a standard in the Bureau of Mines, was taken as a standard and all determinations run against it and checked against each temperature.

Tables and curves are given which indicate that most, if not all, the grain dusts are more inflammable than Pittsburgh standard coal dust, higher pressures being developed in most cases, and especially so at the lower temperatures. The results also seem to indicate that the dusts from oats and yellow corn are more inflammable than those from wheat or other grain. However, the results are only very preliminary, and it is possible that later work will change this supposition, and probably will change the curves, extending them to still lower temperatures.

It is interesting to note the difference in the inflammability of the dried and undried dusts. In nearly every case the pressure developed was appreciably increased after drying. Three are especially noticeable. These gave 0.5 pound pressure or less at 1200° when undried and over 8.0 pounds when dried. Pittsburgh standard coal dust giving 9.0 pounds at the same temperature. This is an indication of what may be expected when the humidity of the air is decreased.

Experiments carried out by the Bureau of Mines² have shown that an explosion could be produced when there was only .032 ounce of coal dust suspended in each cubic foot of air, or one pound in 500 cubic feet of air. In the experiments of M. J. Taffanel, at the Lievin experiment station in France, in one instance as low a weight as .023 ounce of coal dust per cubic foot of space was sufficient to produce an ignition. Since preliminary experiments already conducted indicate that many of the grain dusts have relatively a lower ignition-temperature than many kinds of coal dust and are relatively more inflammable, it may be possible that an ignition of dust of this nature might be produced with a smaller proportion per cubic foot than is necessary for coal dust.

During the investigations it has developed that the following causes have been assigned to many of the explosions in milling plants in this country and abroad:

1. Use of pen lights, or naked flames, such as lamps, torches, gas jets, lanterns, candles, matches, etc.
2. Property fires.
3. Introduction of foreign material in grinding machines.
4. Electric sparks from motors, fuses, switches, lighting systems.

¹Wheeler, R. V. Report on the inflammability and capacity for transmitting explosions of carbonaceous dust, liable to be generated on premises, under the Factory and Workshop Acts, 1913.

²The explosibility of coal dust. Bull. 20, Bureau of Mines, p. 102.

5. Static electricity produced by friction of pulleys and belts, grinding machines, etc.

The investigation has indicated that a large number of the recent explosions and fires have been caused by the introduction of foreign material into grinding machines.

It would appear that a possible means of prevention would be to devise some system by which the foreign material might be removed before it reached the mill. Other preventions suggested are: A complete electric-lighting system, the use of portable electric lamps instead of lanterns or naked lights, the inclosing of the electric-light bulbs in strong wire guards or protectors, and the possible use of vapor-proof globes, and the locating of all fuses, switches, starting boxes, motors, etc., at points where no dust is present. It is also advised to have the receiving bins from the grinding machines as small as practical with the operations, as increased size gives increased space for dust clouds and therefore opportunity for a more violent and destructive explosion.

BY-PRODUCTS FROM PEAT.*

By DR. F. MOLLWO PERKIN.

With the attention of everyone turned today to the production of new fuels and the recovery of by-products from coal and other sources for the use of internal combustion engines or oil-fed boilers, peat as a raw product is naturally being considered.

In Great Britain there are upwards of 6,000,000 acres of peat bog with an average depth of 12 ft. In Ireland there are about 3,000,000 acres of peat bog, some of the bogs being very deep. Peat as dug contains very large quantities of water, generally speaking from 80 to 90 per cent. In this condition, of course, it is of very little use, therefore it has to be, at any rate, partially dried. For the recovery of by-products it is usual to dry it down as far as 20 per cent of moisture—that is if peat coke is to be one of the by-products. Probably each acre would yield from 3,000 to 3,500 tons of such dried peat. Taking the lower figure we arrive at the huge total of 1,800,000,000 tons of peat available in the United Kingdom, and in Ireland, where the average depth is greater, probably nearly as much again.

The great problem in dealing with peat, and the rock on which most of the older enterprises have split, is the removal of the moisture. If wet peat is subjected to hydraulic pressure it is only possible to remove a comparatively small proportion of the water, owing to its being bound up in the cellular structure of the peat. A similar difficulty applies to drying by heat.

Various methods have been used for breaking down the cellular structure of peat and thus obtaining it in a condition in which the moisture can be expelled,

either by pressure or by air drying. Obviously, seeing what an enormous percentage of water is contained in peat, drying by artificial heat alone is out of the question. Generally speaking air drying has been found the most satisfactory, but it is a slow process, and is dependent to a large extent, on atmospheric conditions. The methods most commonly employed on a large scale are:

1. The peat is cut out of the bog by hand or machinery and then air-dried by stacking without undergoing any mechanical treatment.

2. The peat, after being cut out from the bog, is subjected to a macerating process in specially constructed machines.

The methods may be classed under two headings:

- (a) Macerating and adding extra water so as to form a peat slime which can be run into moulds.

- (b) Macerating without the addition of water, then moulding.

By any or all of these processes, however, the difficulty of drying still remains. After maceration the water evaporates very much more freely, but it takes a considerable time for the briquetted peat to lose its moisture down to 20 per cent. Another difficulty is that when the briquets are dried too rapidly they warp and crack.

In Ireland, Scotland and other places, it is employed as a fuel. In such cases, however, it is simply cut into brick-shaped pieces and stacked in such a manner that a large surface is exposed to the air, and it is generally left several months before it is employed as a fuel. Peat prepared in this manner is not suitable for the production of hard coke and by-products, since it is of a more or less porous and spongy nature and occupies too much space.

Peat for the recovery of by-products, therefore, must be treated in such a manner that the cellular structure is broken so that when pressed or moulded it will form a hard briquet.

As already mentioned this may be done by means of macerating machines. A very large number of these have been patented and several of them give very satisfactory results.

Thoroughly pulped peat, when moulded, forms a compact mass with practically no hollow spaces. Such peat, on exposure to the air, dries comparatively rapidly, the drying taking place throughout the mass. After the outside layer has dried it may be exposed to damp weather without further moisture being taken up, the pores close, and moisture is prevented from entering the interior. In dry weather the pores open out again and the drying continues.

The machines for pulping or macerating the peat consist generally of a vertical cylinder or horizontal half cylinder in which knives placed in the form of a screw thread rotate. The raw peat is fed in at one end, and by means of the rotating knives is thoroughly mixed and pulped and carried forward to the other end of the cylinder, where it is extruded in the

*From the Journal of the American Peat Society.

form of a porridge-like mass. Sometimes it passes directly forward by means of a band into a briquetting machine; the briquets are then placed on wooden frames which are piled one above the other in open sheds where they are air-dried.

It is not intended here to go into the merits of the different machines which have been patented and employed for macerating the peat. The cellular structure can, however, be broken down and the water then pressed out hydraulically by other means than maceration.

Even if peat is intended only for fuel, machine-made briquets, that is, briquets made from macerated peat, are far more efficient than when the peat is simply cut and dried. The calorific value is higher and the briquets burn away more slowly. In Holland and in Norway and Sweden machine made briquets are largely used for domestic heating purposes.

Other methods have been tried for breaking the cellular structure and thus obtaining the peat in a condition in which it will dry more readily. Electricity has been used to break down the cells. A plant of considerable size was put down at Kilberry, in Ireland, but unfortunately was not successful. The peat was scooped out of the bog and placed in a rotary hydro-eliminator which removed the surface water. It was then passed through a press and subjected to an alternating electric current. This, it was claimed, broke up the cells, and allowed the water to run out. A number of other electric processes have been suggested.

By a process recently patented, the water is claimed to be rendered expressible by passing an electric current through peat heated to a temperature of at least 100° C. under a pressure sufficient to prevent the formation of steam. The current may be either direct or alternating, although the direct current is preferred. A pressure of 200 volts is slated to be the most economical. Personally I do not think that the difficult problem of eliminating water will be solved by the use of electrical processes.

Other methods are the addition of bleaching powder or limes to the peat, thoroughly mixing and heating to a temperature of 30° to 40° C. The objection of these processes is the large amount of handling they entail, and, it must be remembered, for a peat proposition to be profitable, very large quantities must be worked up. The addition of lime or bleaching powder will also increase the ash content.

Ekenberg found, by heating peat to 150° or thereabout, under pressure, that the cells were broken and that the water could be readily removed.

In a recent French patent it is claimed that if raw peat is simply heated to 60° - 100° and allowed to cool, the moisture can be removed by pressure. In other processes the peat is heated by live steam under a pressure of several atmospheres. The pressure is then suddenly released and the peat dropped into the

receptacle of a specially constructed hydraulic press. On the application of pressure the water content is reduced to about 28 to 30 per cent in the course of a few minutes, that is to say, peat direct from the bog containing 80 to 90 per cent of moisture can be reduced down to 30 per cent in this time. In all these methods, however, the great bulk of the wet peat to be dealt with has to be taken into consideration.

Bacterial processes have also been suggested. In one it is claimed that the bacteria produce hydrogen peroxide which oxidizes the peat and converts it into a condition in which the water is readily eliminated.

CARBONIZATION OF PEAT.

The oldest method of coking peat, which is still to a certain extent employed, is to coke it in heaps in the same manner as the old charcoal burning process, all the by-products being thus lost. The only satisfactory method, and the only one likely to be a commercial success, is to coke in some form of oven and recover the by-products. If, however, a firm, dense coke which will be of value in the metallurgical industry is to be obtained, it is necessary to produce briquets formed from well macerated and dried peat before coking. If there is much moisture then the coke formed will be too porous and friable. An alternative method is to coke moderately dried peat, which need not be briquetted, and to briquet the resulting coke in a manner somewhat similar to that employed in the patent fuel industry.

When peat is coked various by-products are obtained, the quantities and proportions of which depend upon the quality of the peat and the method of coking employed. A peat containing much mineral matter will give a coke which will not be of much value for metallurgical purposes, but this will not to any extent effect the by-products. Peat which contains a high percentage of nitrogen will give a high yield of ammonia. On the other hand the character of the oils will be altered. Generally speaking low temperature carbonization seems to yield the most valuable oils, but there is no reason why the oils should not be driven off at a low temperature, and then, either by moving the partly carbonized peat to a hotter zone in the retort or by increasing the temperature of the whole retort, the maximum yield of ammonia should also be obtained. The first would be a continuous process and the second an intermittent one.

On carbonization of peat the following products are obtained: Gas, oils containing paraffin wax, phenols, ammonia, and small quantities of other bases, methyl alcohol and acetone, acetic acid, pitch and coke.

From the distillation of 576 tons of air-dried briquetted peat containing 31 per cent of moisture at Oldenberg in Germany the following products were obtained per ton of peat. In order to make a comparison I give the results obtained in my laboratory from a Scotch briquetted peat containing about 16 per cent of moisture.

	Oldenberg.	Perkin.
Oils	54.0 lb.	50.0 lb.
Paraffin wax	6.0 lb.	not determined
Phenols	26.0 lb.	28.0 lb.
Methyl alcohol	6.8 lb.	5.1 lb.
Ammonium sulphate	6.2 lb.	30.2 lb.
Calcium acetate	10.0 lb.	8.0 lb.
Pitch	4.0 lb.	3.5 lb.

The Oldenberg peat contained 0.7 per cent of nitrogen and the Scotch peat 2.1 per cent which accounts for the difference in the yield of sulphate of ammonia. Other differences are readily accounted for when it is borne in mind that my results were obtained from the distillation of 5 kilograms of peat at a time, whereas the German results were from 576 tons in quantities of several tons at a time.

The gas having a good calorific value, can be burned under the retorts, and should be sufficient to supply all the heat required when once the process has started. This is shown by the analysis of gases produced:

	Oldenberg.	Perkin.
Carbon monoxide	8.6	14.4
Methane	14.8	11.5
Unsaturated hydrocarbons	1.0	3.4
Hydrogen	23.6	19.0
Carbon dioxide	27.4	31.4
Nitrogen	22.5	19.9
Oxygen	2.2	0.4

The yield of gas is between 5,000 and 6,000 cubic feet per ton of peat carbonized.

The calorific value of the Scotch peat briquets containing 16 per cent of moisture was 8,558 B. T. U., that of the coke produced 13,680 B. T. U.

The tar from which the oils are obtained by distillation is generally considerably contaminated with finely divided carbon which, on distillation, causes further carbonization. A rather brittle pitch is thus obtained if the whole of the oils are distilled off. If, however, live steam is injected towards the end of the distillation a much better pitch is obtained, which can be used for insulating purposes.

The oils obtained in my laboratory consist mainly of saturated hydrocarbons. They have a peculiar burnt peaty odor. This small, however, can be removed by treatment with about 1 per cent of strong sulphuric acid. The lighter oils could be used for internal combustion engines. The heavier oils lack viscosity, so are not of much use for lubricating purposes, but they could be used as oil fuel or might be cracked into light spirit and then employed for automobiles. The phenols, which are obtained in rather large quantities, contain, amongst other products, guaiacol. They have already been employed for making disinfectant bodies and appear to form very good antiseptics.

The Peat, Coke and Oil Syndicate, of Doncaster, carbonize peat containing from 50 to 60 per cent of moisture. The peat is not briquetted previous to being carbonized, the briquetting operation being carried out with the peat coke obtained in the process. This is mixed with certain binding materials, some of which are obtained from the peat by-products. The briquets are then pressed and coked again in the usual

manner. From four lots of one ton each carbonized, the following by-products were obtained:

Water-free crude oils	8.8 gallons
Ammonium sulphate	21.2 lbs.
Spirit (petrol)	3.9 gallons
Spirit 160°-200°	3.5 gallons

Apparently the methyl alcohol and phenols had not been worked up. The paraffin was left in the pitch, which makes a good insulating material. The briquets produced by this process are very hard and have been well reported upon for steel smelting, the average crushing pressure being 812 lbs. per square inch. It is now proposed to erect a plant capable of dealing with 100 tons of coke per week. Preliminary tests have shown that the by-products alone more than cover the whole costs of the process and that the sale of the coke is all profit.

PEAT FOR POWER PURPOSES.

Another method of working up peat and producing by-products is to employ it for the manufacture of power gas. In this respect some very interesting experiments have been made in Canada by the Department of Mines.

In a modified Körting peat gas producer the best results seem to have been obtained with the peat contained from 25 to 30 per cent moisture. With larger quantities of moisture there is great difficulty in eliminating the tar from the gas. It is stated, however, that a peat gas power plant has a distinct advantage over one using bituminous coal. With coal the accumulation of tar in the valves and cylinder is difficult to remove, and necessitates the shutting down of the engine, whereas tar from peat is readily removed by injecting into the open end of the cylinder a mixture of oil, soap and water. This completely dissolves the tar which is thrown out by the forward movement of the cylinder.

The Power Gas Corporation have also a special producer in which peat is employed. In this producer peat containing 50 per cent of moisture can be satisfactorily employed. The company have a special mechanical process for drying peat from 80 per cent to 50 per cent of moisture which renders them independent of weather conditions. It is claimed that by this process the total cost of the peat is only 3s. (72c) per ton including excavating, manufacturing and drying. In all producer processes the peat is completely burnt up, and there is thus no carbon as a by-product. Larger quantities of ammonium sulphate are, however, obtained than by distillation in retorts. On the other hand the tar obtained is less valuable. Given a peat containing a fair proportion of nitrogen, it is claimed that the yield of ammonium sulphate is more than sufficient to pay all working and depreciation costs, so that the power gas is obtained free of cost.

The owners of feldspar properties in the Kingston district of Ontario Province are experimenting in the extraction of potash from ground spar.

THE ORIGIN OF NITRATE DEPOSITS.*

By WILLIAM H. ROSS.†

The origin of all nitrate deposits was at one time accounted for by oxidation. The theory was held that the production of nascent nitrogen through the decomposition of organic matter caused a union to take place between the oxygen of the air and the nitrogen of the organic matter. Since then it has been shown that nitrates may be produced in various ways, and new theories are still being advanced from time to time to explain the origin of the nitrate deposits which occur in various parts of the world. The fact that different views have often been advanced to explain the origin of the same deposit has given rise to a great deal of discussion, and there still exists a wide difference of opinion as to the source from which the nitrogen may have been derived. By the source in this case is usually meant the preceding form in which the nitrogen appeared, rather than the ultimate source of the nitrogen, since this is generally admitted to be the atmosphere. The object of the present writing is to give a review of the various theories which have been advanced in this connection.

The fixation of nitrogen, that is, the transformation of elementary nitrogen into a combined state, may be brought about in the laboratory in a great many ways. Some of these processes have been shown to be profitable commercially, and large quantities of nitrates and other compounds of nitrogen are now being manufactured in Europe, and likewise in Canada, at Niagara Falls, but, apart from those which are experimental, no commercial plants for the manufacture of atmospheric nitrogen products have yet been established in this country. These various processes of fixing nitrogen artificially may be grouped into four classes, according as there is produced (1) nitrates or nitrites, (2) ammonia, (3) nitrides, or (4) cyanamid and its related compounds.

The fixation of nitrogen in nature also takes place in a number of different ways, but, unlike the technical operations just referred to, this is brought about principally by organic processes. Small amounts, however, are also fixed in nature by inorganic processes in a way analogous to some of the artificial methods, and in this way there are formed nitrates or nitrites, ammonia and nitrides.

The best known case of the inorganic fixation of nitrogen in nature occurs when nitric acid is formed in the air by lightning discharges at the time of thunderstorms. The quantity of nitrogen which is combined in this way seems to differ in different parts of the world. In British Guiana during a period of twenty years the quantity so formed amounted each year on an average to 1.88 pounds per acre, while in Utah only 0.356 pound was obtained annually for a period of three years. As a result of the decay of organic mat-

ter on the earth there is usually present in the air a sufficient quantity of ammonia to combine with all the nitric acid formed, although in the tropics the latter may sometimes be in excess. The ammonium nitrate which results from the combination dissolves in the snow and rain, and in this way is carried to the earth along with other ammonium salts. Except in some parts of the tropics the total nitrogen recovered in this way is usually several times greater than the nitric nitrogen formed by the electric discharge. At Rathamsted, England, it amounted on an average, during a period of eight years, to 3.37 pounds per acre annually. At Ottawa, Canada, the average for the past five years amounted to 6.18 pounds per acre.

The quantity of nitrates which is thus formed in the air is small when considered locally, but in the aggregate the amount of combined nitrogen which is thus restored by nature to the surface of the earth is very great and is estimated at about 100,000,000 tons.

Other examples of nitrogen compounds which are not of organic origin are the metallic nitrides and ammonium salts which are found in the vicinity of volcanoes at the time of an eruption. It is probable that they are not carried as such in the fumes of the volcano, but are formed near the surface of the earth through exposure of molten rock to an atmosphere of nitrogen in a way analogous to the manner in which nitrogen is fixed artificially by the Serpek process, which consists in heating an ore of aluminium with carbon in an atmosphere of nitrogen. According to this view, nitride would be formed first, and then ammonia when the former would come in contact with water. Many analyses have been made of the gases given off by volcanoes in different parts of the world, and free nitrogen has always been an important constituent, but so far as known combined nitrogen has never been reported.

A nitrogen compound of inorganic origin is also to be found in the case of a rare mineral which occurs in some parts of Arizona, and which has the distinction of being the only insoluble nitrate occurring in nature. This mineral, to which the name Gerhardtite has been given, is a basic nitrate of copper and is supposed to have formed in the earth by water charged with air percolating over copper ore. It affords an illustration of an unusual way in which the fixation of nitrogen may be brought about.

The organic processes, however, are by far the most important in bringing about the fixation of nitrogen and the formation of nitrates. That nitrogen is one of the principal constituents of plants has been known since the beginning of the last century, but the source of the nitrogen was a matter of controversy for a long time afterwards. The experiments of some investigators showed that with sterilized soil and with all sources of combined atmospheric nitrogen cut off, the free nitrogen takes no part in the food supply of the plant. Other investigators arrived at just the opposite conclusion.

*From the American Fertilizer.

†Bureau of Soils, United States Department of Agriculture, Washington, D. C.

These opposite views led to a great deal of discussion, and it was not until 1888 that Hellrigel was able to account for these conflicting results by growing leguminous plants in nitrogen-free soils. One set of plants was watered with distilled water, while to the other set was added in addition small amounts of leachings, containing only a trace of nitrogen from a cultivated field. The plants watered with distilled water made but a small growth and soon died of nitrogen starvation, but those watered with the leachings reached a full growth and were found to contain about one hundred times more nitrogen than the seed sown. It was observed that the roots of the latter plants were covered with swellings, or nodules, which contained characteristic organisms while those which were watered with distilled water only had none. Furthermore no nodules appeared and the plants did not develop when the soil leachings were sterilized before using.

The experiments thus showed that the plants which were provided with nodules must have obtained nitrogen through the agency of the micro-organisms; that these must have come from the soil leachings; and that they must have the property of fixing the nitrogen of the air. For some unknown reason these bacteria, to which the name *Bacillus radicola* has been given, do not develop on the roots of non-leguminous plants; consequently, when plants of this kind are grown in the soil and harvested, the total quantity of nitrogen present gradually becomes less. The advantage of rotating leguminous plants with crops of this kind thus becomes clear, because when a crop of the former is grown or plowed under as green manure the total nitrogen in the soil is increased. As the plants decay a part of the protein nitrogen of the plant again passes into the elementary state, part changes into ammonia, and a third part changes into nitrates. These changes are brought about by different bacteria, those responsible for the formation of nitrates being called nitrifying bacteria.

The amount of protein nitrogen which is converted into nitrates in the soil by these bacteria varies with conditions and depends on the physical condition of the soil, the quantity of organic matter present, the moisture content and the temperature. A basic element as potash, soda or lime must also be present with which the nitric acid formed may unite. On a limited scale these conditions may be so controlled that large quantities of protein nitrogen may be converted into nitrates as is still done in India for the production of potassium nitrate to be used in the manufacture of gunpowder. The action of the nitrifying bacteria in thus leading to the formation of nitrates does not bring about any increase in the quantity of nitrogen combined, but simply brings about a transformation from one form to another.

Shortly after the discovery that the bacteria which are associated with the roots of leguminous plants are able to fix nitrogen, a great many experiments were made to determine if other bacteria have a similar

function. Very conflicting results were obtained. Some investigators reported that certain bacteria are able to fix nitrogen while others arrived at an opposite conclusion with respect to the same bacteria. Experiments along this line are still being made. It seems that most of the bacteria in the soil do not bring about any fixation of nitrogen, but there is good evidence that there are two or three kinds in addition to the *Bacillus radicola* which are able to do this. Unlike the latter, these bacteria do not require the medium of leguminous plants, but may be active in soils which are devoid of growing vegetation. The most important of these bacteria have been called *Azotobacter chroococcum*. It has also been shown that various fungi, algae and other organisms possess greater or less power of fixing atmospheric nitrogen.

A special study of the amount of fixation which may take place through the activities of these organisms, particularly the *Azotobacter chroococcum*, has been made by Headden¹ and others at the Colorado Agricultural Experiment Station. It was observed that in certain parts of Colorado dark brown spots occur in which nothing will grow. From the color of the spots it was natural to assume that the cause of the spots was due to the presence of black alkali, or sodium carbonate, which is so commonly met with in the soils of arid and semi-arid countries. An analysis of the soils, however, showed little or no sodium carbonate present, but, instead, surprisingly large quantities of sodium, calcium and magnesium nitrates. The spots observed were not fixed, but spread rapidly, and sometimes covered an area of several acres in extent. Moreover, new spots were noticed to appear in old and new localities. In some cases the amount of nitrogen accumulated, as shown by analysis, amounted to as much as 100 tons to the acre-foot. Arguments were given to show that the nitrates could not have originated with the irrigating water nor from concentration of ground water in the surface layers of the soil. That the spots are the remains of great herds of extinct animals, which perished from some unknown cause, was likewise considered improbable, for the reason that the areas involved are too large, and that the spots are increasing in size and appearing in localities where they were never before noted. The theory was therefore advanced that the excessive quantities of nitrates were formed *in situ*, through the nitrogen-fixing activity of micro-organisms in the soil.

It was actually shown that the power to fix atmospheric nitrogen is a property common to many cultivated Colorado soils, and that this power is not confined to nitrogen fixation in solution, but is manifested in soils as well. The principal nitrogen-fixing organisms in the soil were identified as *Azotobacter chroococcum*. These have the power of developing a dark brown color in cultures containing organic matter and a nitrate, but give no color when the nitrate is replaced by organic nitrogen. The rate at which the fixation

¹Colorado Agr. Exp. Station, Bull. Nos. 155, 178 and 179.

took place was considered sufficient to account for the formation of the nitrates found in the soil.

Exception has been taken to this view regarding the origin of these nitrate beds by Stewart and Greaves,² who made a study covering a period of eight years, at the Utah Experiment Station, of the influence of irrigating water upon the production and movement of nitric nitrogen in the soil. Although the soils upon which the investigations were made were ideally adapted both chemically and biologically to support a rapid biological action, no unusual amounts of nitrates were found. A recalculation of the results reported by Headden showed that in the samples, which were taken from the surface of the soil at different points in the same locality, and from the same point at different depths, the nitrates and chlorides varied in the same ratio, and that whenever an accumulation of the former took place during a given period, the latter also increased during the same time in the same general proportion. It was therefore concluded that the excessive quantities of nitrates formed in the soils of Colorado were not formed *in situ*, but owe their origin to the same source as the other water-soluble salts.

Further investigations by Headden,³ however, showed that, while large amounts of chlorine generally occur with excessive nitrates, this is accidental rather than necessary, and that on the whole there is no relation between the amount of nitrates and that of any other class of salts present. Additional evidence is given to show that the concentration in nitrates in brown spots in which nothing will grow is not due to the accumulation of pre-existing nitrates, but to the action of micro-organisms which are able to bring about the fixation in the soil of atmospheric nitrogen, and that the dark brown color which is characteristic of the spots is due not to black alkali, but to the development of pigment by the organisms.

The occurrence of nitrate deposits in caves has long been known. During the War of 1812, and again at the time of the Civil War, the "saltpeter" deposits in the Mammoth Cave and in other caves in Alabama and Georgia formed an important source of nitrates required in the manufacture of gunpowder. The origin of these deposits is commonly ascribed to the decomposition of animal remains, and particularly to the excrements of bats. In the Southwest small deposits of guano are still to be found in some caves, but almost all deposits which are sufficiently large to be of commercial value have been removed for use in the manufacture of fertilizers. Samples taken from some of the caves where the guano has undergone decomposition have been analyzed by the writer and found to run as high as 75 per cent of potassium nitrate. Other samples have been examined which consisted of very pure elongated white crystals of calcium nitrate, and which had been taken from crevices in a cave. When placed

in a humid atmosphere, these soon melt in the moisture which they absorb from the air, but may be kept indefinitely in a desiccator.

While guano is usually considered to be the source of the nitrates found in caves, other theories are occasionally advanced to explain the origin of some of the deposits. Thus Hess⁴ considers that guano could not be the source of the large store of nitrates which have been taken from the Mammoth Cave at distances of over five miles from any opening which leads to the surface since bats go, as a rule, but a short distance from the entrance to the cave. Moreover, in the bottom of many caves there are to be found earths from which nitrates can be extracted, but which do not contain an animal remains as would be expected if the nitrates were derived from guano. To explain the occurrence of nitrates in caves of this kind, the view is put forward that the nitrates do not come from guano, but originate in the surface soil above the caves through the oxidation of organic matter by nitrifying bacteria. As the soil in limestone regions is usually loose and porous the nitrates are considered to be carried down by percolating water and deposited in the floor of the caves. Air currents in and out of the caves would remove the water by evaporation, and the nitrates would consequently remain, and would not be washed away so long as the inflow of water did not exceed that lost by evaporation.

A similar explanation is given for the origin of nitrate deposits under over-hanging cliffs. Thus water carrying nitrates dissolved from the soil percolates through the earth and a portion finally oozes out at the surface underneath where it evaporates and leaves the nitrates behind. Being protected from the rain in this position the nitrates in this way are enabled to accumulate.

The theory advanced by Hess to account for the origin of nitrates in caves has not met with universal acceptance. Nichols⁵ has argued that bats do frequent remote parts of caves; that cave earth does contain organic matter; and in that the proportion of phosphates to nitrates in the cave earth is much too great to be accounted for on the supposition that they were brought in by percolation from the surface soil. It is considered that while small deposits may be found in the way described by Hess, the great bulk of the nitrates that are found in caves results from the decomposition of bat guano. By leaching of the soluble salts from the guano, the nitrates are removed and may be concentrated in other parts of the cave or distributed elsewhere.

Because of their solubility it is not to be expected that any large accumulation of nitrates can take place excepting in protected places such as caves, or in arid countries where there is very little rain. In such countries, however, there is very little vegetation, and consequently the organic processes which are of such im-

²Utah Agri. Exp. Station, Bull. No. 114.

³Colorado Agri. Exp. Station, Bull. No. 186.

⁴Journal of Geology, 8, 129 (1900).

⁵Journal of Geology, 9, 236 (1901).

portance in bringing about fixation of nitrogen in humid countries are able to operate to a much less extent in desert regions. We thus find that in the soil of such regions the total nitrogen present is usually much less than in soils which support a good vegetation.

On the other hand, the soils of desert countries have marked nitrifying powers with the result that a large percentage of the nitrogen actually present is converted into nitrates. Furthermore, owing to the low percentage of organic matter present and to the porous nature of desert soils the anaerobic denitrifying bacteria are not so active in changing nitrates into free nitrogen, while the lack of vegetation prevents their conversion into protein nitrogen. The nitrates which are formed are thus enabled to accumulate and either remain in the soil or are transferred by underground waters to other localities where they may be concentrated by evaporation of the water at the surface of the ground. If there has been any introduction into desert localities of organic matter from external sources, as may be brought about by the droppings or remains of animals, the accumulation of nitrates may be correspondingly increased. It thus happens for the reasons given that the largest nitrate deposits are found in desert regions.

In this country few nitrate deposits are to be found apart from those of cave origin. The most extensive so far known occur in San Bernardino and Inyo counties, California, along the shore lines or bed beaches of what was supposed to be a former sea, but which is now geologically known as Death Valley. The region popularly known as Death Valley is that portion of the valley proper which is below sea level. The territory covered by nitrate beds has been estimated to cover an area of about 35,000 acres. Through erosive agencies the clay beds in which the nitrates were deposited have been worn into buttes and ridges of characteristic shape and color. The hills so formed vary from only 50 ft. high to over 300 ft. Samples taken from the niter-bearing strata in the hills, and exposed by erosion, vary all the way from a trace to more than 50 per cent of nitrates. It is generally agreed that these deposits have not been formed *in situ*, but have resulted from the concentration of nitrates formed from the decomposition and nitrification of animal and plant life which must have existed in the region at the time that the valley was filled with water. Owing to the limited distribution of these nitrates they are not considered of much commercial importance and the same may be said of all other deposits so far discovered in this country.

Small nitrate deposits are also to be found in various other parts of the world as in the Sahara, in Russian Turkestan, and in Egypt where nitrate earths occur which contain about 15 per cent of calcium and sodium nitrates. The earth has long been used locally as a fertilizer and its use is supposed to be increasing. The source of the nitrates in this region is not known.

All known deposits, however, which occur, like the ones just referred to, in various desert regions through the world are insignificant compared with the well-known deposits in the deserts of Atacama and Tarapaca in the north of Chile. These deposits command a great deal of interest, not only on account of their commercial importance, but also for the many attempts which have been made to explain why the quantity of nitrates in this particular region should be so large compared with any other known deposit.

The first shipment of nitrates to Europe from Chile was made in 1825. Since then the annual exportation has continuously increased until in 1912 the total quantity exported amounted to 2,485,860 tons of which 1,925,590 tons went to Europe, 469,100 tons to the United States, and 91,170 tons to other lands.

The arid region in which the nitrates are found extends for about 430 miles between 13° and 25° south latitude and lies between the Andes in the East and the Coast Range on the West. This area lying between the two mountain ranges does not form a continuous valley, but is broken up by transverse ranges into a series of elevated basins or plateaus. These plateaus are generally flat or undulating and have an elevation from less than 2,500 ft. to more than 5,000 ft. They have a general slope from the foot of the Andes towards the Coast Range, and as a result the lowest part of this plateau region, or pampa as it is called in Chile, lies along its western border where it joins the foot hills of the Coast Range. It is along this zone that the nitrate deposits occur. The surface of the surrounding region is dry and sandy and vegetation is totally absent. The nitrate beds as they occur in different parts of this region vary in thickness up to about 6 ft. They are usually found at or near the surface, but may in some cases be covered with an overburden to a depth as great as 30 ft. The nitrate deposits are never found pure, but are always mixed with sodium chloride and other salts, and are impregnated with insoluble earthy material. Crude nitrate may sometimes run as high as 60 to 70 per cent of sodium nitrate, but a deposit running 50 per cent is considered high grade material. Material containing less than 16 per cent is too low grade to be mined at a profit at present.

The source of these deposits is a subject which has given rise to a great deal of discussion. Many theories have been advanced to account for the origin of the nitrates, but all appear to fall short of adequately accounting for all the conditions under which the nitrates are found in Chile. It is generally considered that an organic source is the most probable, but there have not been lacking explanations for the formation of these nitrates which have been based on inorganic agencies.

Thus one of the theories advanced is that the nitrates may have resulted from electric storms occurring in the Andes. It has been suggested that the nitric acid which is formed in this way by the oxidation of

the nitrogen of the air becomes changed into calcium nitrate in coming in contact with the limestone of the mountains, and that this in turn on being washed down into the pampa region has been converted into sodium nitrate on coming in contact with the sodium salts already existing there. It has also been stated that at certain seasons of the year there is a great deal of static electricity in the air over the desert region owing to the strong winds and the extremely dry climate, and that the nitric acid which is formed as a result of this condition is carried to the ground by the moisture in fogs which drift in from the sea.

The view has also been advanced that the nitrogen in the Chilean nitrate may have come from nitrogenous fumes given off by volcanoes in the Andes. It has already been pointed out that nitrides and ammonium salts are sometimes found in the vicinity of volcanoes after an eruption, but whether these compounds result from the direct fixation of atmospheric nitrogen near the mouth of the volcano, or from some combined form of nitrogen already present in the earth is not known, but the former view is the more probable. It has been shown, however, that the source of the nitrogen is not organic.

It has been claimed by some that alkali carbonates are able to bring about the fixation of atmospheric nitrogen into nitric acid in the presence of oxidizable matter, and Pissis⁶ expressed the opinion that the niter beds in Chile were formed in this way. It was pointed out that the decomposition of feldspar rock in the region of the Andes supplied alkali carbonates while the protoxide compounds of iron which are common in the rocks of the pampa are easily oxidized under ordinary conditions to form peroxide compounds of iron. The view was accordingly put forward that the alkali carbonates in contact with rocks of this kind brought about the oxidation of the nitrogen of the air with the ultimate formation of nitrates.

Perhaps the most far-fetched attempt at an explanation of the origin of these deposits was that presented by a writer⁷ in the *Comptes Rendus* a few years ago. It was observed that pieces of glass left on the ground in the vicinity of the saltpeter mines in the Province of Aconcagua, Chile, became colored blue in a short time, while samples of the same glass exposed on the roofs of buildings to the direct rays of the sun remained colorless. This suggested the possibility of the soil in the vicinity being strongly radioactive, which was thought to be confirmed by the action on photographic plates properly protected and subjected to an exposure in the ground for a month. It was suggested that the radioactivity of the soil as indicated by these experiments might have had something to do with the formation of nitrates in this part of Chile. It is now known that all soils are slightly radioactive and to approximately the same extent.

None of these views which have suggested an inor-

ganic mode of formation for the Chilean nitrates has received very general acceptance. Much more credence is given to the theories that the nitrates found in the deserts of northern Chile have resulted from the decomposition of organic matter brought into the basins in which they are found from outside sources.

One of the most popular of these theories suggests seaweeds as the source of the nitrates. The explanation is given that in past ages the pampa regions were sea beaches, and that an enormous amount of seaweed was piled upon them. In course of time the beaches were elevated above sea level, and the collected seaweeds in decaying under arid conditions decomposed in such a way that the nitrogen present was converted into nitrates, and the iodine into iodates. It may be pointed out in this connection that immense groves of giant kelps are now to be found along the Pacific Coast of North America, and that the proportion of iodine to potash in the dry plants is about the same as is to be found in the crude niter of Chile. The ratio of nitrogen to potash in the former, however, is very much less than in the latter.

There are many objections which may be offered to this theory. Thus, if the niter came from seaweed it must necessarily contain bromine as well as iodine, since both are present in this source, and there is no known natural process which can bring about the separation of bromides and iodides. So far as known, however, bromine has not been found in any of the nitrate deposits of Chile; whereas, from analyses made by the writer, the bromine in the giant kelps of the Pacific, for example, is of the same order as the iodine.

Again, sea shells are never found in the nitrate beds, and the stones in the neighborhood are sharp and jagged and show no signs of being worn by water as they must necessarily have been if they had at one time existed on a sea beach.

Perhaps the best known theory which has been advanced to explain the origin of these nitrates is that they have been derived from the decomposition of ancient guano deposits. In defending this theory Penrose⁸ has assumed, in the same way as those who favor a marine origin for the nitrates, that the pampa region was once a part of the ocean bottom, but as the region gradually rose it became a more or less inclosed basin. At this time guano beds were supposed to have been deposited along the borders of these waters, just as they are now deposited in the neighboring shores of the Pacific. It is considered quite possible that marine plants might also have collected in the basin at the same time, and that these constituted the source of the iodine, although it is pointed out that this element might also have originated in minerals, or mineral springs occurring in the region. The formation, as suggested, of inland basins of sea water, which would ultimately evaporate, would furnish also a source for the common salt associated with the nitrates, as well as for the soda of the nitrates.

⁶"Nitrate and Guano Deposits in the Desert of Atacama," A. Pissis, London, 1878.

⁷Bordas, *Compt. rend.*, 147, 924 (1908)

⁸*Journal of Geology*, 18, 1 (1910).

The guano theory, however, has been objected to on the ground that no accumulation of phosphate has ever been found in the nitrate country, and such must necessarily occur in amount corresponding to the nitrates if the latter have been derived from guano. It is argued, on the other hand, that such phosphates may actually exist, but that they have not yet been discovered, and it is further explained that the absence of the remains of birds and of sea shells may be accounted for on the ground that sufficient time has elapsed since the beds were deposited to admit of the decay of all such materials.

There is still, however, a further objection which applies to both the seaweed and guano theories. Thus, if the region was at one time a sea beach it must have taken ages, as Newton has pointed out, for the nitrate pampa to be elevated to its present level. During these ages the region must have passed through varying climatic conditions, including most probably rains. It has therefore been argued that the nitrate deposits are, geologically speaking, of very recent origin.

In suggesting another organic source from which the nitrates may have been derived, Kuntze has called attention to the fact that vicuñas, and llamas which are at home in this portion of the Andes, have the peculiar habit of always depositing their manure in one and the same place. Immense herds of these animals are supposed to have roamed over the region from time im-

chiefly responsible for transporting and concentrating the nitrates from the superficial layers of the pampa soil to the lower western part of the pampa region where the deposits are found. The nitrate deposits are thus looked upon as the concentrated fertility of the thousands of square miles of land between the watershed of the Andes and the Coast Range. It is admitted that electrically generated atmospheric nitrate may also be present.

Headden¹⁰ has suggested that the nitrates of Chile may have been formed by the direct fixation of the nitrogen of the air by nitrogen-fixing bacteria in the same way as accumulations of nitrates have been shown to have been formed in certain soils in Colorado.

It is apparent from the views which have thus been advanced to explain the origin of the Chilean nitrates that no single theory has yet been proposed which is adequate to account for all the conditions under which the deposits are found, and it seems most probably, as some have suggested, that instead of being formed in one way only, the nitrates owe their origin to several sources.

GERMAN POTASH SUPPLY.

The Department of State, according to the Daily Consular and Trade Reports, is in receipt of a telegram from the Netherlands legation, under date of

TABLE I.—IMPORTATIONS OF POTASH INTO UNITED STATES DURING THE PAST THREE FISCAL YEARS.

	1912.		1913		1914.	
	Tons.	Value.	Tons.	Value.	Tons.	Value.
Kainit	485,132	\$2,399,761	466,795	\$2,154,977	541,846	\$2,579,619
Manure salts	192,738	1,814,071	171,802	1,794,058	261,342	2,767,241
Muriate of potash	215,957	7,235,718	201,220	6,782,056	237,916	7,915,523
Sulphate of potash	44,476	1,826,836	42,745	1,753,485	45,139	1,897,740
Total	938,303	\$13,276,386	882,562	\$12,484,576	1,086,243	\$15,160,123

memorial, each herd having a definite dunging place at some convenient point. As the manure accumulated its nitrification would progress rapidly under the prevailing arid conditions. The common salt would be derived from the urine and excrements, while the decomposition of rocks throughout the region is considered sufficient to account for all other salts occurring in the crude niter.

Newton⁹ is of the opinion that the source of the nitrates is the organic matter occurring in the soil of the great plain lying between the nitrate beds and the Andes. It is pointed out that there exists in this region all the conditions which favor the rapid conversion by nitrifying bacteria of the nitrogen of organic matter into nitrates. The soil is porous and basic in its nature, and contains organic matter chiefly of ancient vegetable origin; the temperature is high and, on account of the absence of rain, there is no growing vegetation to absorb the nitrate, and therefore it must accumulate. The mountain floods which swamp the plain once in every seven or eight years are considered

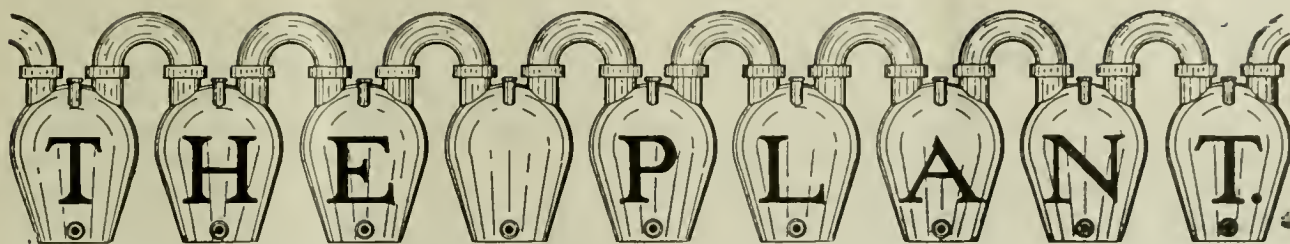
August 31, to the effect that the embargo on the exportation of potash from the Netherlands has been temporarily removed.

The world's supply of potash comes from Germany, and one of the chief routes for shipping it has been down the Rhine and through ports in Holland. Owing to the war in Europe this neutral territory would be the only outlet for German potash. Importations into the United States of this article in its various forms during the past three fiscal years ended June 30 are shown in Table I.

During the six months ended June 30, 1914, the imports of cocoa beans into Havre, the most important market for this product in Europe, reached the unprecedented total of 339,809 bags, as compared with 236,917 bags in the corresponding period of last year. In fact, the former figure is nearly equal to the imports for the entire year 1913, namely, 359,093 bags, although last year was above the average.

⁹Jour. Soc. Chem. Ind., 19, 408 (1900).

¹⁰Colorado Agr. Exp. Station, Bull. No. 155.



**THE MANUFACTURE OF ETHYL ALCOHOL
FROM WOOD WASTE—PRELIMINARY
EXPERIMENTS ON THE HYDROLYSIS
WHITE SPRUCE.***

By F. W. KRESSMANN.

THE PRESENT VALUE OF WOOD WASTE.

The value for most of the wood waste produced today is limited to its fuel value for the production of power at the mill. In some cases, methods of closer utilization have been worked out, but compared with the total amount of wood waste produced, the amount of material so utilized is almost negligible. Furthermore, most of the large lumber mills produce waste greatly in excess of the amount necessary for power production and the waste burners are still in use, involving not only a loss of large amounts of wood, but also a definite fixed charge to get rid of it. The utilization of this material is limited, due to a number of considerations which may be classified as follows:

(1) Large Bulk—The bulkiness of the waste material makes a minimum amount of handling imperative and almost prohibits its transportation.

(2) Mechanical Condition or Form—The mechanical condition or form of the waste is one of the greatest stumbling blocks to its more complete utilization. Sawdust and shavings are too finely divided to be of value for paper and pulp production or for destructive distillation. For the former, the fiber length has not only been reduced, but the fibers have also been torn and lacerated much as in the production of mechanical ground wood. The destructive distillation of sawdust and shavings is not practicable for two reasons: First, the small size of the material makes it such a poor conductor of heat that it is impossible to char it completely in the ordinary forms of retorts and kilns in use; second, the charcoal produced is so finely divided that it is difficult to cool and handle and there is no ready market for it. In addition, the waste, as it comes from the mill, is usually a mixture of all the forms enumerated above and any attempt at a separation other, perhaps, than a simple blowing or screening to remove the very fine stuff will increase the cost of the raw material to a prohibitive figure, as shown by the experience of several pulp and paper mills in the yellow pine region of the south. A satisfactory process, therefore, for the utilization of wood waste should be able to handle practically any and all forms of waste as they happen to come from the mill.

(3) Non-Homogeneity and Non-Uniformity—Except in some cases, as in factories using only one or two species of wood or in some mills manufacturing only a few species, as, for example, the "yellow pine" (longleaf, shortleaf, loblolly) mills of the south, the non-homogeneity of the waste has operated against its efficient utilization, for many processes such as pulp and paper or destructive distillation require particular species to give a yield and quality of product that will make the processes commercially feasible.

THE VALUE OF WOOD FOR ALCOHOL PRODUCTION.

All woods, however, have one point in common and that is the fact that they all contain more or less cellulose which makes up the fibers of the wood along with an incrusting substance called "lignin." Any process which could chemically utilize this cellulose would, therefore, overcome the objections laid down above as the form of the material, length of the fiber, species, etc., would not be a consideration since finely divided material would permit of a quicker and more complete reaction and coarse material could readily be reduced to a finer condition.

The production of sugars and ethyl alcohol from cellulosic materials such as straw, linen, cotton, peat and wood, in fact, all plant fibers, has engaged the attention of chemists and technologists for nearly a century, although it is only within the last two decades that serious attempts have been made to utilize wood waste by this means.

The principal sources of fermentable sugars from which alcohol is derived at present are:

1—Hydrolytic products of starch.

2—Sugars from fruits; sugar factory residues, such as molasses, etc.

The cost of the raw material for alcohol derived from such sources, however, has been so high that alcohol had not been able to compete in certain fields where its properties and worth are recognized. The technical application in the arts and industries is gradually increasing, due to a rather liberal denaturing policy which has permitted special denaturants for special industries, but its use in this country as a source of liquid fuel is comparatively limited and it is this field that offers greatest possibilities in the future. A study of the motor fuel problem will show that the production of mineral fuels such as gasoline, motor spirits, etc., is not keeping pace with modern automobile production, and alcohol appears to be the only solution of the problem, for if alcohol can be produced from wood waste at a reasonable figure a tremendous supply of raw material is not only available at present

*Paper presented at the 49th Meeting of the American Chemical Society, Cincinnati, April 6-10, 1914, and reprinted in the Journal of Industrial and Engineering Chemistry.

but will continue to be so in the future from a natural growing raw material which is not a foodstuff.

PROCESS.

The process of producing ethyl alcohol from wood consists, in general, of digesting sawdust or hogged and shredded wood with a dilute mineral acid at from 60 pounds and more of steam pressure. This converts part of the wood into a mixture of pentose and hexose sugars. The latter are then fermented, producing alcohol.

The processes using concentrated sulphuric acid, in which the wood is really attacked and dissolved by the acid as in the Ekström¹ process, have not received commercial attention, notwithstanding the fact that Flechsig,² many years ago, showed that cotton cellulose could be converted into dextrose and alcohol almost quantitatively thereby. The more recent work of Willstätter³ and Feichmeister has confirmed these results with fuming hydrochloric acid, but in all cases the amounts of acid have been so large compared to the process in which the acid is used merely as a catalytic agent, that the large initial and recovery costs for acid have prevented commercial development.

The source of the fermentable sugar, that is, whether derived from the cellulose or lignin of the wood, has long been a mooted question and has been the occasion of considerable investigation, but the fact remains that a wood cellulose like soda of sulphite pulp will produce about twice as much fermentable sugar and alcohol as the original wood, the yields being proportional to the cellulose content.

HISTORY.

The earlier work in the field from the time of Braconnot in 1819 until the work of Simonsen⁴ in 1898, although exceedingly interesting historically, may almost be disregarded so far as its scientific value is concerned. It contains many inaccurate and impossible statements, and many contradictions, and is in many cases very vague in regard to yields.

Simonsen carried out the first systematic investigation of the subject in which the effect of different variables such as the amount of water, pressure, temperature, amount of acid, and time of inversion were studied in some detail. As shown later⁵ by Neumann, Simonsen's work is also contradictory in some cases, due mainly to the fact that only a single experiment under each set of conditions was made. In his work on a large scale he was in general unable to duplicate the results obtained in the small autoclave cooks. The yields of alcohol varied considerably, although under the most favorable conditions he obtained in a few exceptional cases yields which were higher than those obtained on the small scale (6 per cent of dry weight of sawdust).

Since Simonsen published his work and took out patents on his process practically all over the world, the production of ethyl alcohol from sawdust has received considerable attention and a large amount of money has been spent in its technical development. Four plants have been built in this country, but none of them up to the present are considered to have achieved commercial success.

OUTLINE OF EXPERIMENTAL WORK.

Although other investigators have duplicated Simonsen's yield, which is about 6 per cent by weight in alcohol of the dry weight of the wood, no systematic study has been made reinvestigating the variables studied by Simonsen, except the work of Cohoe in which hydrochloric acid was used as the catalytic agent instead of sulphuric.

The data to be presented in this paper are the result of the first part of a systematic study of the variables in this process carried on at the Forest Products Laboratory and cover the first two of the following:

- 1—The influence of pressure and temperatures of digestion.
- 2—Length of time of digestion.
- 3—Ratio of water to dry sawdust.
- 4—Concentration of catalyzing agent in the water.
- 5—Ratio of catalyzing agent to dry sawdust.
- 6—Size of the sawdust, hogged slabs, etc.
- 7—Effect of adding catalytic agent (acid) after preliminary heating of the wood.
- 8—Effect of varying amounts of bark in the sawdust, or, more specifically, tannins, etc.
- 9—Special chemical treatments other than acid catalysis, or in addition to catalysis.
- 10—A study of the fermentation variables.
- 11—Steam consumption per ton of sawdust inverted.
- 12—Variations of yields from different species and mixtures.

EXPERIMENTAL APPARATUS AND PROCEDURE.

The apparatus used and method of procedure in each experiment were as follows: A rotary digester consisting of thin cast-iron inner shell lined with acid-proof enamel, and an outer shell of steel, the two being separated by several inches from each other, was used for the digestion. The internal length of the inner shell is about 5 feet, and the diameter about 2½ feet, making a total capacity of about 22 cubic feet. Steam is admitted to the inner shell and space between the inner and outer shell simultaneously, the digester being similar to a steam-jacketed apparatus except that the inner shell is removable and can readily be taken out and replaced. After a cook has been completed the digester is blown off, the blow-off vapors being condensed in a quartz coil. A cast-iron tank also lined with acid-proof enamel is connected to the digester so that its contents may be introduced into the digester when the latter is under pressure. This tank is used for acid storage and mixing. The steam flows to the inner shell and space between the two shells through separate pipes; the one leading to

¹French Patent 380,358, German Patents 1913,112, 207,354.

²Z. phys. Chem., 1882.

³Ber., 1913, 2401.

⁴See E. Simonsen, *Zeitschrift für angewandte Chemie*, 1898, 195, 962, 1007; Theor Körner, *Ibid.*, 1908, 2353; Neumann, *Dissertation*, Dresden, 1910.

⁵Neumann, *Dissertation*, Dresden, 1910.

the inner shell also connects with acid tank. All pipes in contact with acid liquor or acid vapor are enamelled and valves are of special bronze so as to reduce corrosion to a minimum and to avoid complications in fermentations due to the presence of iron, copper, and zinc salts.

The pressure is taken by means of a gauge protected from the acid vapors, and temperatures are taken on a recording thermometer, the bulb of which projects into the sawdust in the digester.

The digester is filled and emptied through a pair of concentric manholes in the inner and outer shell. The usual procedure is to load the digester with sufficient sawdust to be equivalent to about 100 pounds of dry dust. The exact weight and moisture content are recorded. The diluted acid is then added, the manhole covers

so had drained off the digester was rotated so that the manholes were at the bottom and the sawdust was raked out. In the later experiments this sawdust was then centrifuged.

Both the digester liquor and treated sawdust were weighed and analyzed for acidity, total solids, dextrose, etc.

The treated sawdust was next placed in the leaching tank, where the remainder of the sugar was extracted from it with warm water. The liquor from the digester and leaching tank was then neutralized with calcium carbonate and allowed to settle. The clear liquor was then concentrated in a single effect vacuum evaporator to a concentration of 10 to 15 per cent sugar for fermentation. The liquors were usually saved until the concentrations from two or three runs were obtained. Where possible, these were divided into two or more parts and fermented with brewers' yeast under varying conditions.

RESULTS.

Sugar Yields.—Figs. 1, 2 and 3 show the effect on yield of varying the pressure and time of cooking. The curves give the yields in total sugar instead of alcohol, since the fermentation end of the work is being taken up in detail at present and was not standardized at the time these experiments were made so as to give check results. The greatest variations on duplicate digestions made with sawdust from the same batch was only 0.11 per cent of total sugar, so the sugar data may be accepted as fairly accurate.

In each run the amount of sawdust used was very nearly equal to 100 pounds dry material; the amount of acid added was the same in all, 2.00 pounds of 90

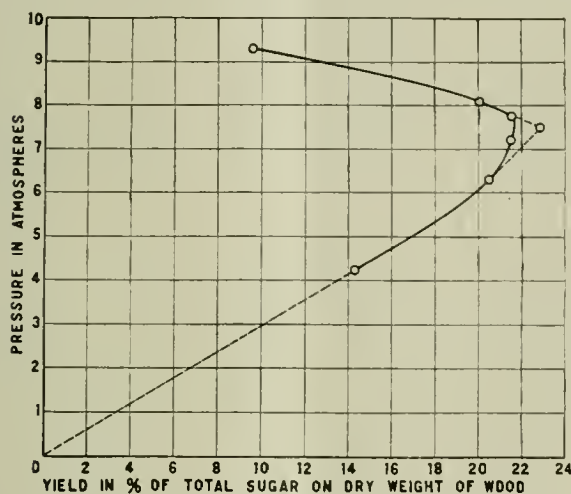


Fig. 1—Variation of Yield of Total Sugar with Pressure of Digestion. Cooking Period, 15 Minutes.

hotted on, steam admitted, and rotation begun. Before the temperature reaches 100° C., the air in the inner shell and space between the two shells is vented so as to get a more accurate gauge reading. The admission of steam is continued, until the desired pressure is reached, after which the steam is throttled to maintain that pressure for the desired length of time.

At the completion of the latter (or, in cooks of 15 minutes or more, two or three minutes before the time was up) the rotation was stopped and the vapors were then blown off and condensed as rapidly as possible. The time of blow-off varied somewhat, depending on the pressure at which the cook was made and the total amount of liquid and sawdust in the digester. The condensing and cooling capacity of the coil was not equal to the demands placed upon it so that the blowing off of the digester took much longer than it should (about two hours from 7 to 8 atmospheres to atmospheric pressure).

The condensed blow-off was weighed and analyzed. The steam which condensed between the two shells was drained out and weighed. It was also tested qualitatively for dextrose to detect any leakage from the inner shell. The liquor in the inner shell was drained out. After as much of the liquor as would do

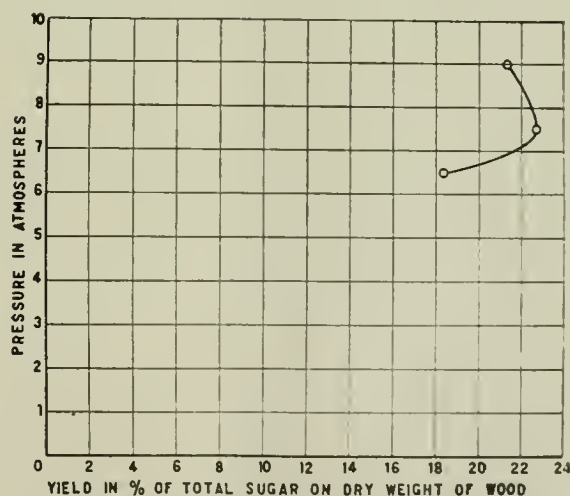


Fig. 2—Variation of Yield of Total Sugar with Pressure of Digestion. Cooking Period, Zero Minutes.

to 95 per cent sulphuric; and the amount of water in all cases at the end of the cook was equal to four or more than four times the dry weight of wood used. The ratio of acid to dry wood was about 1.8 per cent, while that of water to dry wood was 400 per cent or more. Many of the charges were made up so that the initial amount of water present was exactly four times the dry weight of the material. These,

however, showed no change from others in which the amount of water added was allowed to vary within certain limits.

Fig. 1, with a cooking period of 15 minutes, shows a decided maximum in yield at a temperature equal to 7.5 atmospheres steam pressure.

A new lot of sawdust was used for part of the work which included the cooks at 7.5 atmospheres and

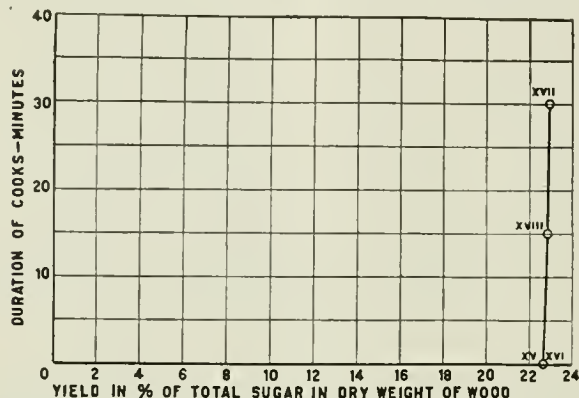


Fig. 3—Variation of Yield of Total Sugar with Varying Periods of Digestion. Cooking Pressure, 7.5 Atmospheres.

which probably accounts for the increase in yields shown at that point and which has been indicated by the dotted lines.

On comparing the yields shown in Fig. 1 with those of Simonsen a much greater decrease in yields at pressures above 7.5 atmospheres was noted. From the work of Neumann it is known that dextrose decomposition is very rapid above 175° C., which corresponds very closely with 7.5 atmospheres pressure, in addition to this decomposition, however, the reaction seems to be reversible at this pressure, a fact which has not been recognized heretofore.

Fig. 2, with a cooking period of zero minutes (blowing off as soon as the pressure is reached), shows the same pronounced maximum at the same pressure and also shows a smaller decrease in yield at high pressures. Using the pressure of 7.5 atmospheres as a constant (at which the best yields were obtained as shown by Figs. 1 and 2) and varying the time of cooking, as shown in Fig. 3, practically no increase or decrease in yield of sugar is shown; in other words, the rates of formation and decomposition of the sugars formed at this temperature are the same and, therefore, maintain a constant yield of sugar. At higher temperatures, however, the rate of decomposition seems to be decidedly greater than the rate of formation which was shown in Figs. 1 and 2. In Fig. 1 the curve crosses the abscissae corresponding to 9 atmospheres at a point showing a yield of 14 per cent of sugar, while in Fig. 2 the yield of 9 atmospheres was 21.20 per cent of sugar. This decided difference in sugar values shows clearly the injurious effect of increasing the time of cooking, especially at pressures greater than 7.5 atmospheres.

The injurious effect of increased time of cooking is also shown in several other ways; the sawdust, of

course, is rotated longer in the longer cooks and more fine stuff is formed which makes leaching and handling more difficult. The sawdust is also more friable and larger amounts of fine stuff were formed while being stirred in the leaching tank. And finally, as shown, by the ratio between sugar and total water-soluble solids, more of the sawdust was attacked so that the amount of extraneous water-soluble material other than sugars was greater.

Cohoe⁶ was the first one to state that given the proper adjustment of the various phases the reaction is practically instantaneous and our work is in entire agreement with this statement.

Volatile Acid Yields.—In addition to the sugars formed as a result of hydrolysis, acetic and formic acid are also produced, probably from a splitting off of acetyl and formyl groups in the lignin complex. The yield of acetic acid has been fairly constant over a wide range of cooking conditions averaging 1.42 per cent of the dry weight of the wood. This is of particular interest not only because of its influence on the subsequent fermentation of the neutralized extract but also because it is practically the same yield obtained by destructive distillation of the wood. Numerous observers such as Klason, Büttner, and Wislicenus have shown that this decomposition does not take place until a temperature of 280° C. or more has been reached, whereas the temperatures of hydrolysis in this work have averaged 100° C. less than that. The

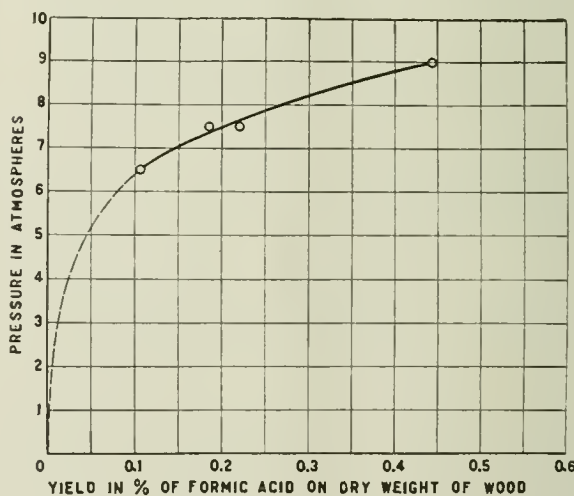


Fig. 4—Variation of Formic Acid Yield with Pressure of Digestion. Cooking Period, Zero Minutes.

yield obtained, however, is in very close agreement with the work of Bergström,⁷ although the latter used no acid, merely hydrolyzing with 4 parts by weight of water, at 6 atmospheres pressure for two hours.

The yield of formic acid, however, varies with the cooking conditions as shown by Fig. 4, the amount increasing with increasing cooking pressure. Increasing the time of cooking also materially increases the yield, for as shown at 7½ atmospheres and a zero-minute cook the yield is about 0.2 per cent, while at

⁶Jour. Soc. Chem. Ind., 1912, 513.

the same pressure for a 15-minute cook the yield is about three times as great (0.58 per cent). This increase in formic acid production also shows the rate of sugar decomposition since formic acid and levulinic acid are both products of such decomposition. The exact amount hydrolyzed from the wood is difficult to determine since it is also a product of sugar decomposition. Bergström obtained 0.19 per cent at 6 atmospheres cooking for two hours with water alone, whereas we have obtained that figure at $7\frac{1}{2}$ atmospheres in zero minutes but only 0.105 per cent at 6.5 atmospheres in zero minutes. Technically, the yield of formic acid is of importance because of its influence on yeast growth.

Numerous patents granted in this field have discussed the value and recovery of the volatile acids produced. To show the distribution of the various acids, the amounts actually contained in the liquor drained from the inner shell, the condensed blow-off and moist sawdust, were calculated in percentages of the total amount of each acid produced. The results are given in Table I:

TABLE I.

Cook	Percentage of Total Volatile Acid in						Total amt. of volatile acid in per cent of dry weight of original wood	
	Inner shell liquor		Condensed blow-off		Moist digested sawdust			
No.	Acetic	Formic	Acetic	Formic	Acetic	Formic	Acetic	Formic
XV...	62.0	62.1	2.6	2.1	35.4	35.8	1.22	0.185
XVI...	48.5	49.4	5.7	5.9	45.8	44.7	1.62	0.220
XVII...	37.8	41.0	9.5	4.3	52.7	54.7	1.48	0.570
XVIII...	40.2	46.2	7.2	7.0	52.6	46.8	1.32	0.598
XIX...	35.0	32.6	6.8	6.1	58.2	61.3	1.60	0.443
XX...	49.5	39.2	6.3	5.9	44.2	54.9	1.25	0.105

The average amount of acetic acid recovered in the blow-off was 6.4 per cent of the total, and 5.2 per cent of the total amount of formic acid produced.

With an average yield of 1.42 per cent of acetic acid, this would be equivalent to 1.81 pounds of acetic acid per dry ton of wood and since the average concentration of acetic acid in the condensed blow-off was only 0.20 per cent, commercial recovery is obviously out of the question.

Alcohol Yields.—As mentioned heretofore, the fermentation work on the experiments outlined in this paper had not been standardized. Ordinary brewers' yeast, a bottom yeast, has been used without attempting to acclimate it to the mashers used. The main difficulty encountered was the slowness of fermentation which, in some cases, permitted infection of the mashers with wild growth. It was found, however, that the latter could be controlled and excluded by judicious sulphiting and for this purpose potassium metabisulphite⁸ was used. Various forms of organic and inorganic nitrogen nutrients were used, of which freshly killed yeast (boiling for two minutes in part of the mash) and ammonium nitrate seemed to be the best.

Table II gives part of the results obtained:

TABLE II.

Cook No.	Total reducing sugars		Fermentation efficiency	Yield of alcohol		Yield of alcohol in U. S. gallons of absolute alcohol per dry ton of original wood
	per cent of original dry wood	Per cent of total sugars fermented		per cent by weight of original dry wood	per cent	
II....	21.50	68.63	89.59	6.76		20.35
V....	21.54	71.27	91.49	7.18		21.63
XVII..	22.95	69.27	88.70	7.22		21.70
XVIII.	22.85	55.5	96.2	6.24		18.75
XX....	18.34	65.25	85.42	5.24		15.80
XIII...	18.81	59.20	83.93	4.78		14.90
XIV...	20.29	46.05	65.05	3.11		9.35
XII....	11.58	55.24	68.87	2.25		6.8

Some of the above results, however, do not represent the yields obtainable under ideal conditions since many of the fermentations were retarded or spoiled entirely due to experimentation on fermentation conditions.

Under improved conditions with a yeast specially propagated the yields undoubtedly could be materially increased.

SUMMARY.

I—The maximum yield of sugar was obtained at a pressure of 7.5 atmospheres and above and below this point yields decreased very rapidly.

II—A cooking period of zero minutes, that is, blowing off from 7.5 atmospheres as soon as that pressure is attained, was the most advantageous for sawdust.

III—Increasing the time of cooking did not increase the yield and greatly influenced the mechanical condition of the sawdust with greater subsequent difficulty and cost of handling. Economically speaking, the yield decreased as the time of cooking increased.

IV—Using white spruce sawdust as a raw material, from 22 to 23 per cent of the dry weight of the wood was converted into sugar. About 70 per cent of this sugar was fermented with an alcohol yield of over 91 per cent of the amount theoretically possible to obtain from the fermentable sugars. Calculating these yields to a tonnage basis, between 21.63 and 21.70 U. S. gallons of absolute alcohol were obtained per dry ton.

V—Under a rather wide range and variation of cooking conditions of hydrolysis, white spruce yielded about 1.4 per cent acetic acid, showing, therefore, a parent substance (lignin?) of a comparatively definite acetyl content.

VI—The yield of formic acid varied with the conditions of hydrolysis. In cooks longer than zero time, the formic acid yield was indicative of hexose decomposition rather than increased formyl hydrolysis.

Salt production in the United States during 1913 totaled \$10,000,000 in value, or double that of 10 years ago.

⁸Der Papierfabrikant, 2, 305.

⁸See "Biological Investigations," F. T. Bioletti and W. V. Cruess, Bull. 230, Agr. Expt. Sta., Berkeley, Cal.

DYESTUFF MANUFACTURE IN AMERICA.*

By J. M. MATTHEWS.

As is known, the large majority of the dyes at present employed in this country are manufactured in Germany. There has been considerable mention made of the establishment of the dyestuff industry in this country owing to the fact that we have available large quantities of raw material. As nearly all the dyes are made from coal tar, and as coal tar is derived from the distillation of coal for the production of illuminating gas, it would be the impression off-hand that we could quickly ourselves utilize our coal tar products.

A little careful consideration of this question, however, causes us to somewhat revise our first judgment in the matter; considerable difficulties confront us although they can all be overcome.

While it is true that this country produces large quantities of coal tar, it is also true that we are not very large producers of benzol, and its consumers which form the real basis of the dyestuff substances. Benzol is a liquid of rather low boiling point and consequently of a volatile character, sometimes called benzene, but which is not to be confounded with petroleum, naphtha, or benzene, the latter being a very different chemical substance. Benzol is obtained by the distillation of coal tar which itself is produced by destructive distillation of coal in retorts. When bituminous coal is heated in a closed retort, large quantities of gaseous products are evolved, together with a considerable amount of a dark peculiarly smelling liquid, while there is left behind in the retort a solid residue known as coke. The gas and the liquid distillates are separated from each other by scrubbing and washing, and the gas is used for illuminating gas. The liquid coal tar can be subjected to further distillations between varying ranges of temperature, and in this manner there is obtained a series of distillates running from the first light oil distillate to the heavy oils, and a black substance is left undistilled, known as pitch.

The character of the coal employed and the method of conducting its distillation cause wide variation in the quantity and nature of the constituents present in coal tar. The coal tar obtained by present American methods of distillation is capable of yielding but a very small quantity of benzol and anthracene, two of the principal raw materials used as a starting point in the manufacture of coal tar dyes. We will have to change our system of producing illuminating gas so as to leave the proper kind of tar. This will eventually permit a greater profit even to the gas maker, besides giving the dyestuff maker the ingredients which he needs. While our coal tar does not yield much benzol and anthracene, it does yield a large quantity of naphthalene, a substance which is familiar to most people under the form of tar camphor or moth balls, and naph-

thalene can be employed for the production of indigo and a few other dyestuffs but it does not find any very extensive use outside of the indigo colors.

There are in this country several establishments where some coal tar dyestuffs are produced, but nearly all of these depend on Europe for most of their raw materials and intermediate products, and should these supplies be cut off they would be in a very poor condition to supply even to a small extent the requirements of the textile trade.

It is fortunate that logwood is largely manufactured in this country, and there is no doubt that sufficient logwood dyestuff could be produced by our domestic factories to meet all demands. This dye is extensively used for the dyeing of black silk and in some degree for black cotton and wool. It is also possible that a considerable quantity of aniline salt can be produced here which would take care of a good portion of our aniline black dyeing on cotton piece goods and hosiery; but for the great majority of colors, especially the fast colors for wool and cotton, the present outlook is not by any means promising. We will have to develop a dyestuff industry of our own.

The most important dyestuff is indigo, for without doubt this single dyestuff is employed in larger quantity than any other. At the present time a very large quantity of our supply of indigo is made in Germany from coal tar, this product having, to a large degree, displaced the natural indigo formerly obtained by extraction from the indigo plant. The indigo made from coal tar is identical with that from the plant and is in a much higher state of purity. It is also brought into trade in a form which is more readily adapted to the dyeing process. The natural indigo was usually sold to the buyer in the form of rather large blocks or lumps, and it had to be ground in special mills in order to reduce it to a very fine state of division, as only in this form can it be employed in the preparation of the dye vat. The indigo prepared from coal tar and known as synthetic indigo, in the process of its manufacture is obtained in a very fine state of division, and this is made up in the form of a paste so as to prevent the formation of lumps and is available to the dyer in this form. We have in this country large quantities of naphthalene available for the production of indigo, but foreign patents would stand in the way of our making this color economically. We will have to revise our patent laws, compelling foreign patentees to produce in this country. Further, we must develop our own methods of production. It is true that, no doubt, the suppression of the synthetic indigo making would stimulate very largely the cultivation of natural indigo which chiefly comes from India and the East Indian islands, and it is probable that our supplies of indigo could be largely drawn from this source. During the last few years, however, the acreage of indigo under cultivation has been very widely reduced owing to the material decrease in price through competition with the synthetic indigo.

*From Daily Trade Record.

TESTS ON ELECTRIC FURNACES FOR BRASS FOUNDRIES.*

By DR. HERBERT G. DORSEY.

Although no brass foundries are melting their product electrically at the present time on a commercial scale, yet it seems probable that within a few months several companies will be nearing the solution of this problem.

Although electric furnaces have been applied successfully to the steel industries for many years, little attention has been paid to electric furnaces for brass melting until the last two or three years.

Since induction furnaces and arc furnaces have been successful in the steel industry, it was natural that they should also be tried for brass melting. The induction furnace of the ordinary horizontal ring type soon proved to be impracticable for melting of any of the metals or alloys of high conductivity, such as aluminum, copper, or brass. The heat generated being proportional to the resistance multiplied by the square of the current, if the resistance of the bath of metal is very low, the current itself must be enormously great in order that the necessary amount of heat may be generated. But the pinch effect, or squeezing together of a current carrying liquid conductor, also depends upon the square of the current and for such high currents the pinch effect actually opens the circuit if used on any of these three metals. For this reason, this type of induction furnace was soon eliminated from the field of brass melting.

Some advocated the arc furnace, but as the results which had been obtained by this method did not look very favorable, it seemed best for The National Cash Register Co. to try out some of the resistance types of furnaces.

A search through the literature showed only one advertisement of an electric furnace which was claimed would melt brass. This was the Helberger type furnace made by the Allgemeine Elektrizitäts Gesellschaft of Germany, which advertised furnaces up to 100 kg. capacity, and their largest type furnace was ordered in August, 1912.

Little real information could be learned about the details of this size furnace, although some of the smaller furnaces had been previously described in various places. The furnace is outlined in Helberger United States patents No. 932,986, and No. 1,023,309, and some of the details are described in German patents. Apparently this large size furnace has been developed from a small size suitable for such work as dentists and jewelry work. The development, however, does not seem to have been accompanied by practical experience for it seems that a small furnace of this type might be worked successfully.

After a year and a half of waiting, the furnace was received and a still further delay was encountered be-

cause no tilting device had been provided with the furnace. Although the advertising literature showed a tilting device, none was received and a cablegram to the makers brought the reply that none was furnished with the furnace. A tilting device was made so that the furnace could be operated by hand, the larger part of the weight being counterbalanced.

As received, the furnace consists essentially of two parts, a 100 k. w. transformer to convert 440 V. single phase, 60 cycle alternating current down to various voltages from 6 to 12, and the furnace proper. The secondary of the transformer is water cooled and the current is carried by means of thin strips of copper to two water-cooled copper blocks on either side of the furnace. Sliding copper brushes make contact with these blocks and heavy copper strips carry the current to the top and bottom of the furnace.

Figure 1 shows a cross section of the furnace which consists of the resistor I, made of carbon and

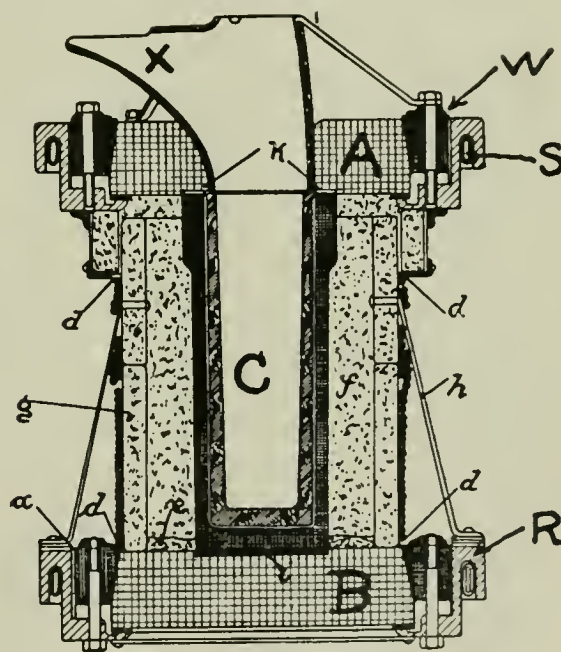


Fig. 1.

resting on a carbon block B. The resistor is 30 in. high, 11 in. in diameter at the bottom, and 13 in. at the top. The conductivity of the resistor and top and bottom plates is about the same as that of ordinary electric light carbon. Around this resistor is a magnesite filling F which is retained by the fire clay cylinder G, and the latter is wrapped with asbestos rope D. Above the resistor is a carbon ring A, which serves to keep the resistor in place and also supply an electrical connection. Current from the sliding brushes is carried to the cast iron rings R at the top and bottom of the furnace which are water-cooled by means of annular openings S, contact being made between the carbon rings A and B by means of wedges W. As the furnace was originally received, these wedges were graphite, although an extra set made of cast iron were sent with the furnace. There seemed to be no dif-

*Paper presented at the Annual Meeting of the American Institute of Metals, September 7-11, 1914, at Chicago, Ill.

ference in the operation whichever material was used. The upper carbon ring A, the lower carbon plate B, and the resistor are all held together by means of three long bolts fixed with screws and nuts geared together so that the adjustment of clamping may be changed if necessary. Inside of the resistor I and fitting it snugly is a crucible C made of a composition of low electrical conductivity, sort of a carbon clay mixture somewhat similar to a regular foundry crucible material. At the top of the furnace is a pouring spout X made of perforated sheet iron covered on either side with a mixture of graphite and fire clay. The shape of this spout makes it difficult to close the crucible.

The furnace part is supported on trunnions in such a manner that it may be tilted, having the axis of rotation through the lip of the furnace so that when metal is poured, it may be poured directly into molds. The trunnion supports were so weak that it was necessary to brace them to prevent lateral motion. The heat of the furnace is generated in the carbon resistor, already described, and must travel through the walls of the crucible before it can reach the metal to be melted. The crucible itself must be a very poor conductor of electricity even when hot, otherwise the current would pass through the metal, the latter being such a good conductor of electricity compared with the resistor that little heat would be generated unless enormous currents are used.

The transformer is provided with a switch leading to different taps of the primary so that six different voltages may be applied to the resistor. The following table shows the ratios of the primary voltage, amperage and kilowatts, the measured voltage of the secondary and the computed current flowing through the resistor, assuming 96 per cent transformer efficiency:

	Primary		Secondary	
	Voltage	Amperage	K.W.	Voltage Amperage
1st	462	65	30	6.6 4450
2nd	455	79	36	7.2 4660
3rd	458	96	44	8.0 5280
4th	447	123	55	8.9 5940
5th	437	160	70	10.1 6660
6th	422	218	92	11.5 7680

Current was first turned into the Helberger furnace on Jan. 14th, and the furnace warmed up a little bit each day until Jan. 17th, when it was brought up to a temperature of 1275° C. Then a number of melts were taken as shown in the following table:

Date.	Heat No.	Time.	Amt. of Metal Temp. pounds.	C.	K.W.H. per cwt.
1-17-14	1	64 min.	121.5	1330°	85 70
1-17-14	2	33 min.	120	1325°	51 42
1-19-14	3	81 min.	200	1250°	111. 50.5
1-19-14	4	48 min.	200	1300°	76.5 38
1-19-14	5	41 min.	200	1380°	65.5 33
1-20-14	6	70 min.	200	1260°	108.5 54

During the sixth run, the current fluctuated considerably when the metal was stirred and the circuit breaker was thrown out twice indicating current upwards of 300 amperes. Carbon monoxide flames were seen rising around the upper part of the crucible. On pouring the metal it continued to run out after the crucible part was apparently empty, just as though the

crucible had been punctured and metal had run in between the crucible and resistor. On removing the crucible the next day, breaking it to pieces to get it out, a plate of whitish-colored metal about 3/16 in. thick was found between the bottom of the crucible and the resistor. On analysis this metal showed silicon and aluminum which were not present in the "C" metal which had been melted.

A new carbon crucible was inserted and melting continued on Feb. 3d, 4th and 5th, as follows, but no record was kept of runs seven and eight, "L" metal being melted Feb. 3d and 4th, and "E" metal Feb. 5th:

Date.	Heat No.	Time.	Amt. of Metal Temp. pounds.	C.	K.W.H. per cwt. day avg.
2-3-14	9	42 min.	150	1270°	52
2-3-14	10	40 min.	150	1270°	48
2-3-14	11	37 min.	150	1270°	43
2-3-14	12	29 min.	150	1270°	24
2-3-14	13	55 min.	170	1270°	56
2-3-14	14	60 min.	200	1200°	39 27
2-4-14	15	143 min.	150	1200°	120

Date.	Heat No.	Time.	Amt. of Metal Temp. pounds.	C.	K.W.H. per cwt. day avg.
2-4-14	16	49 min.	150	1270°	55
2-4-14	17	40 min.	150	1200°	51
2-4-14	18	30 min.	150	1200°	39
2-4-14	19	32 min.	150	1200°	50
2-4-14	20	30 min.	180	1270°	42
2-4-14	21	42 min.	165	1200°	40
2-4-14	22	34 min.	150	1270°	55
2-4-14	23	31 min.	150	1200°	50
2-4-14	24	36 min.	150	1200°	48 35.6
2-5-14	25	132 min.	150	1170°	128
2-5-14	26	42 min.	175	1200°	64
2-5-14	27	44 min.	150	1170°	43
2-5-14	28	56 min.	150	1170°	45 44.8

The crucible having worn thin and cracked through, a crucible was molded in place, around a core of wood. A mixture of two parts carborundum and one part fire clay was very slightly moistened and rammed into place until it appeared homogeneous. After drying slowly and thoroughly, heats No. 29 and No. 30 were successfully made as follows:

Date.	Heat No.	Time.	Amt. of Metal Temp. pounds.	C.	K.W.H. per cwt. day avg.
2-16-14	29	234 min.	150	1175°	160
2-16-14	30	53 min.	175	1135°	67 70
2-16-14	31	Metal froze			

This freezing of the metal was caused by poor contact between the upper carbon plate and the wedges which carried the current from the circular metallic conductor to the carbon plate. The molded crucible was then removed and a new crucible, new resistor and new top plate, all from the makers, were installed and eighteen successive heats made as follows:

Date.	Heat No.	Time.	Amt. of Metal Temp. pounds.	C.	K.W.H. per cwt. day avg.
2-23-14	32	159 min.	150	1175°	139
2-23-14	33	40 min.	150	1200°	67
2-23-14	34	32 min.	150	1175°	56
2-23-14	35	41 min.	150	1175°	50
2-23-14	36	30 min.	150	1200°	46
2-23-14	37	93 min.	150	1175°	44
2-23-14	38	44 min.	175	1175°	80
2-23-14	39	22 min.	150	1240°	51
2-23-14	40	20 min.	150	1200°	38 41.5
2-24-14	41	154 min.	150	1175°	175
2-24-14	42	40 min.	150	1200°	67
2-24-14	43	32 min.	155	1175°	62
2-24-14	44	30 min.	150	1240°	60
2-24-14	45	31 min.	150	1175°	33

2-24-14	46	70 min.	150	1175°	28	
2-24-14	47	37 min.	170	1240°	72	
2-24-14	48	32 min.	170	1175°	51	
2-24-14	49	30 min.	156	1200°	45	42.2

At this time the crucible wore out and another crucible was made of carborundum sand and fire clay and six heats were obtained as follows:

Date.	Heat No.	Time.	Amt. of Metal Temp.		K.W.H. per cwt. day avg.
			pounds.	C.	
2-26-14	50	70 min.	150	1175°	106
2-26-14	51	45 min.	150	1175°	65
2-27-14	52	127 min.	150	1175°	193
2-27-14	53	55 min.	165	1230°	70
2-27-14	54	42 min.	170	1175°	69
2-27-14	55	40 min.	162	1175°	53

The last of these heats indicated foreign matter in with the metal and an analysis showed it to contain silicon and aluminum. When the furnace was again dismantled a whitish metal was found in the bottom which contained 5.22 per cent silicon, 0.42 per cent iron, and 0.70 per cent aluminum, none of which were present in the alloy being melted.

Considered commercially, from our standpoint this furnace is a failure. It shows many disadvantages and very few advantages. As a laboratory furnace, including experimental work in the foundry on new combinations, it possibly is a good type of furnace, provided a suitable crucible can be obtained, because almost any temperature may be reached and easily maintained for any considerable length of time, and if only a few heats were to be made per week, the occasional renewing of crucible, resistor, plates, etc., would not be bothersome. To prevent contamination of the metal, some other crucible material would be necessary. On 55 heats, five different crucibles were used on an average of only eleven heats per crucible. Working at the above basis no more than 11 or 12 heats could be melted per day unless the furnace were operated at night which would mean a new crucible every day. Unless an air blast were used, to cool it, the furnace would scarcely get cool enough during the night to insert the crucible the next morning. Assuming ideal conditions it would require about thirty-one kilowatt hours per cwt. to melt the metal, while the above tests show about sixty-two kilowatt hours per cwt.

Another disadvantage of the furnace is the fact that the crucible is long and narrow and it is difficult to charge the metal in any quantity unless the furnace tender stayed right with it and put it in piece by piece. This would mean that it would require one tender for each furnace which would be rather expensive. In a more convenient form, the crucible would be a short cylinder of large diameter, but electrically this would be bad as it would necessitate greater currents.

These tests seem to eliminate the Helberger Furnace in our own foundry as a competitor with pit fires. We are now working with other types of furnaces, but have not yet had trials enough to reach any conclusions.

THE BUREAU OF MINES' EXHIBIT AT THE PANAMA-PACIFIC EXPOSITION.

The United States Bureau of Mines is planning a comprehensive exhibit at the Panama-Pacific Exposition.

In arranging the exhibit, the bureau has had in mind, not only the value of interesting those engaged in the various mining and metallurgical industries, but also the education of the general public to a better knowledge of the magnitude of these industries and to the efforts which are honestly being made by the miners and mine operators, with the assistance of the Bureau of Mines, looking toward a more safe conduct of mining and a more efficient utilization of the products of the mines after they are won from the earth.

The bureau's exhibit is located in the Palace of Mines and Metallurgy. An automatic duplex projecting machine will continuously show lantern slides illustrative of the activities of the bureau and simultaneously give descriptions of the lantern slides.

Nearby will be shown the layout of a model hospital, including a receiving room, ward room and operating room, fully equipped for demonstrations by the United States Marine Hospital Service; also a model of a change and wash house, another welfare feature which is being installed at modern mining and metallurgical operations. A plan of an ideal mining town will be shown.

First-aid demonstrations will be given frequently. An air of reality will be lent to the demonstration by the removal of apparently injured men from the exhibition mine beneath the building by helmet and rescue crews.

A complete display of rescue apparatus and safety lamps will be given in a glass smoke-room. Tests of safety lamps will be made, showing their tendency, under unfavorable conditions, to ignite explosive gas, and also showing methods of testing for explosive gas by means of their caps. An exhibit of the physical and chemical characteristics and constituents of explosives is being arranged.

Visitors going through the exhibition mine will regain the surface through the radium booth in which actual radium emanations will be shown. Surrounding this radium booth, there will be complete exhibits of the various radium ores and of radium products. The metallurgy of various products will be shown by a comprehensive exhibit.

An officer of the bureau will give his whole attention to visitors. Copies of the bureau's publications will be available for free distribution to visitors who may be particularly interested.

This exhibit, in connection with the exhibition mine immediately beneath the bureau's space, should be interesting and instructive to those engaged in the mining industry and to the general public.

METALLURGY.

A RATIONAL TEST FOR METALLIC PROTECTIVE COATINGS.*

By J. A. CAPP.

SUMMARY.

It is proposed to test metallic protective coatings such as those applied to iron and steel by galvanizing, sherardizing, lohmanizing and other processes, by exposing the articles to an atmosphere saturated with salt water. The saturated atmosphere is produced by projecting into the test chamber an atomized spray of water saturated with common salt in solution. Poor coatings break down in from 2 or 3 hours to 24 hours, while efficient coatings stand up at least a week. Failure is indicated by the development of red rust.

There are several processes commercially used for covering the surfaces of metals easily corroded or rusted, such as iron in its several forms, with other metals less easily corroded, or with metallic oxides. These may well be called "metallic" protective coatings in distinction from the types of coating which are in the nature of paints or their equivalent.

The object of the application of these metallic protective coatings is to enable the coated articles to resist atmospheric exposure without rusting for a longer time than they could withstand such exposure without protection. Obviously, then, the only final test of the efficiency of a given type of coating is actual exposure to the same sort of influences that the material is supposed to resist in service. If the coating is at all efficient, this takes so long a time that more rapid methods of determining relative efficiencies become a necessity. The most commonly used methods of testing such metallic protective coatings are those of chemical attack, which in effect measure either the thickness or the weight per square unit of the protective coating. Such methods of chemical attack permit the comparison of results obtained from tests upon the same sort of coating, but difficulty is encountered when attempt is made to compare the results obtained by such tests on one sort of coating with those obtained on another character of coating. For instance, the well-known Preece test yields excellent comparative results on galvanized coatings. When, however, it is used for coatings applied by the sherardizing process, the results are not at all comparable. Neither is the Preece test applicable to coatings of tin or of lead. In the case of sherardized articles, it has been suggested that the coat, which is a combined structure of zinc and zinc oxide, together with some zinc-iron alloy, be removed in strong alkalies which will not attack the iron be-

neath. This would enable one to determine the weight of coating per unit of surface calculated to metallic zinc, but experience has shown that the results do not necessarily indicate the efficiency of the coat, and that it is not easy to determine the relative proportions of zinc and zinc oxide. Furthermore, comparison of the efficiency of a sherardized coating with ordinary galvanizing is not possible when the sherardized coating is tested by solution in a caustic alkali, while the galvanized coating is subjected to the Preece test.

Some years ago, when testing electrical insulation such as is used for overhead line construction, we found that material which stood fairly well when immersed in water failed badly when exposed to the weather, especially if exposed during a hard rain. This led us to produce a rain in the laboratory by sending a stream of water through an ordinary rosette such as is used with a gardener's watering can. The results were encouraging, but too severe, because the individual streams played steadily on one spot and produced erosion. Then we tried an atomizing nozzle, projecting a cloud of moisture into a chamber in which the test specimens were exposed; the results were better, but there was still a possibility of some wear if the article was directly in the path of the stream and near to the nozzle. The problem seemed to be solved when care was taken in placing the articles to keep them out of the direct path of the jet issuing from the atomizing nozzle. As experience was gained with this type of test, as applied to insulating material, it was found that what seemed to be the essential requirement was the maintaining of an atmosphere substantially saturated with moisture; and this saturated-atmosphere exposure has been one of the tests regularly applied to all insulating materials intended for outdoor use since it was first worked out some fifteen years ago. It has been found to give reliable indications of the ability of insulation to resist weather, except, of course, as such ability is affected by extremes of heat and cold, erosion from the wind carrying dust particles, etc.

The problem of determining the resistance of protective coatings to weather corrosion is very similar to that of testing insulations for their weathering qualities. The conditions of exposure are the same, and hence there seemed to be no essential reason why the saturated-atmosphere test would not apply equally well to protective coatings as to insulation. Tests were begun several years ago to try out the method, and the only fault found with it was that it was somewhat slow. Good coatings did not show any signs of breaking down after several weeks of continuous exposure to the fog; yet there was encouragement in the fact

*Paper presented at 17th annual meeting of American Society for Testing Materials.

that bare metal began rusting in a few hours, and rust spots began developing on poorly protected surfaces in from a few days to a week.

The fact that more trouble is experienced with trolley-line suspensions along the seashore than with the same devices inland, led immediately to the trial of an atmosphere saturated with salt water, with astonishingly satisfactory results.

As now used, the test consists in exposing the articles in any convenient chamber into which there is projected an atomized spray of water saturated with common salt in solution, care being taken to avoid placing the test specimens directly in the path of the jet. To insure constant saturation, an excess of salt is kept in the water at the bottom of the chamber. The spray is produced by a jet of compressed air lifting the water to the nozzle, whence it is projected as a cloud. This apparatus is the common atomizer, so-called, used in the household. The chamber is necessarily not tightly sealed, but is open sufficiently to permit "breathing"; when used with an air jet, there is a slight pressure which is relieved through the breathing openings. If desired, the test may be modified by the use of a fine steam jet to raise the temperature of the atmosphere in the chamber. There is also the possibility of rendering the test atmosphere slightly acid or alkaline by suitable additions to the water in substitution for the salt. For use with plain water, the closet generally used for cement testing does very well, provided care is taken that it is so arranged as to maintain the air practically at 100 per cent relative humidity. When using salt solutions, recourse must be had to the atomizing jet to insure the development of the salt fog.

When exposed as described, articles have a very thin film of moisture over their surface, but there should be very few, if any, drops of sensible size on the objects. Obviously, the test is very searching, as all parts of the surface are exposed, and any pin holes or uncovered areas become evident. This gives one an opportunity to learn something of the efficiency of any protecting process in taking care of edges, sharp corners, porous spots in the metal surface, etc. By noting the character of the final general break-down, a very good idea of the evenness of the coating applied may be obtained.

The method of test may be applied to bare metals as well as to those coated to prevent rusting. For this purpose, the plain saturated atmosphere is apt to be better than a salt atmosphere, because the latter may be too severe and hence make comparisons rather difficult.

The salt-spray test, as we have called it, has been used in the laboratory with which the author is connected for a number of years, and during the last four or five years it has also been used commercially as a check upon the process of sherardizing which is in use. The coated articles are exposed to the salt fog, and are examined from time to time to note their surface condition. When the coated material is iron in any of

its several forms, red rust begins developing as soon as the coat breaks down. This rust may appear in small pin points which gradually extend, or it may appear generally over the surface of the article. When the coating is relatively thin and poor, rust may develop in from 2 or 3 hours to 24 hours, or longer. A better coat will last 2 or 3 days, but a well-applied coat of requisite thickness will last at least a week. If no rusting is developed in two weeks' time, it may safely be assumed that the life of the coating will be practically indefinite. These figures are based on experience with both sherardized and galvanized types of coating. Other types give results which lie in approximately the same range.

This method of testing is not offered in replacement of other methods of testing which have long been in use, especially when such tests are used solely for comparison on material treated always by the same process. It has, however, almost entirely displaced all such methods of test in our own practice, especially when comparisons are desired between processes of different character, because it is the only test which we have been able to devise which approximates practical conditions, and yet yields results within a reasonably short time. The salt-spray test is only an exaggeration of what may be expected at the seashore and differs only in degree, not in kind, from the normal conditions under which the article is intended to be used.

The area of forest land in Japan is said to be approximately 50,000,000 acres, or almost half the area of the country, and state-owned forests comprise about 40 per cent of the forested area. The empire is so well adapted to the development of forestry that, as facilities for communication improve, a steady increase is expected in the revenues derived from this source. The estimated revenues from the government forests for the fiscal year ended March 31, 1914, are \$5,360,000, while the expenditures for the same period are given as \$2,327,000. Provision has been made for extensive improvements in administration, and subventions have been granted for the afforestation of waste public lands. Meteorological observatories are to be established.

In order to increase the demand for cotton, one of the largest flour-milling firms in America has directed its managers and salesmen all over the country to urge its customers to accept deliveries of flour that are shipped in cotton instead of jute sacks. Hitherto jute imported from India has been used extensively for shipments of flour, both to home and foreign markets. The sacks employed hold 140 pounds each. If the trade can be induced to accept shipments in cotton sacks holding 98 lbs. each, there will be a marked increase in the demand for home-grown cotton, and the action of the flour-milling firm is regarded as a long step in this direction.

PROGRESS IN THE NOMENCLATURE OF ALLOYS.*

By G. K. BURGESS.

Since last year's meeting of this institute, which endorsed the suggestion to take up the subject of standard designations for alloys, careful attention has been given to the matter in several quarters. The most important and far-reaching event in this connection has been the first report to the British Institute of Metals of its Committee on the Nomenclature of Alloys¹ on which were representatives of six other British technical societies.

The editor of the International Journal of Metallography, Dr. Guertler, has invited discussion of alloy nomenclature in that journal and has himself published a very comprehensive paper² on the subject.

Mention should also be made of a paper by Moellendorf³ on nomenclature and standards for bronzes, as well as of the summary of the history and properties of brasses and bronzes containing manganese⁴ by our Secretary, Mr. Corse, and Mr. Skillman, which helps to clarify the confusion concerning the terms manganese bronze and manganese brass.

There are two fairly distinct aspects of this nomenclature question. First, we have to consider the naming of the alloys themselves in terms of their component chemical elements or otherwise, and second, the naming of the metallographic constituents which are recognized as accompanying certain chemical or physical properties of the alloy and characterizing the distribution and relation of the elements to each other in the alloy. Or, in short, it is necessary to provide names for the composition of an alloy and for the arrangement of the constituents in the alloy. Although in general they are distinct, there may arise overlapping in the nomenclature of the alloys and their metallographic constituents, so that both aspects of the subject should be kept in mind when either one is being specifically considered.

The report to the British Institute of Metals is confined to the first phase of the subject, the naming of the alloys, and lays down the following guiding principles:

"(1) So far as names intended for use in industrial and commercial practice are concerned, it is desirable to adhere to existing names sanctioned by long usage as far as possible, provided that all such names can be so defined as to avoid all risk of confusion or ambiguity.

"(2) The coining of new names or the adoption of recently coined names not in general use should be avoided as far as possible.

"(3) It is desirable to employ simple English names throughout, avoiding the use of Latin or foreign names, and of chemical or other symbols."

The principle adopted for the construction of a system of nomenclature "is that of denoting any alloy by the names, in English, of its component metals, placed in the order of increasing numerical importance from the point of view of chemical composition by weight." When two or more metals are present in nearly equal amounts they should be placed in alphabetical order. "Where an alloy consists of more than three metals its systematic name shall not as a rule contain more than the names of three metals present in the largest proportion by weight, but the presence of additional metals or elements shall be denoted by the prefix 'comp' or 'complex.' If, however, an alloy of this kind contains an intentionally added element which, although present in small quantity, gives the alloy a distinctive character, that element may be named first."

The report ignored the question of tolerances and considered as beyond its province the question of impurities and specifications.

Two very important classes of alloys are named: (1) "The term *brass* is to be used as an abbreviation of the words 'zinc-copper' as employed in the systematic nomenclature. Thus when the word 'brass' alone is employed it shall denote an alloy of zinc and copper only, containing more copper than zinc, i. e., containing over 50 per cent of copper. When an alloy containing a third metal, such as tin, is to be denoted, the name of the additional element shall be used as a prefix, precisely as in the systematic nomenclature. Thus an alloy containing tin 1 per cent, zinc 29 per cent, and copper 70 per cent, would be called 'tin-brass.'"

(2) Similarly the term *bronze* is held to mean "tin-copper."

The Advisory Committee to the Bureau of Standards on non-ferrous alloys, comprising representatives of this institute, the A. S. T. M., the American Chemical Society, and the American Institute of Mining Engineers, at a meeting held on April 14, together with representatives of that bureau, considered the British Committee's report, and it was the opinion of those present "that this report was conservative and satisfactory so far as it went, although it contains one recommendation not in accord with general practice in the United States, namely the order of names in an alloy to be in order of increasing numerical importance. It was the consensus of opinion of the committee that it would be highly desirable for the American Societies interested and the Bureau of Standards to co-operate with the British Institute of Metals in this question of nomenclature of non-ferrous alloys."

It will be noted that there are many points of resemblance between the principles laid down in the British report and the suggestions made by Mr. Karr in a paper⁵ presented at last year's meeting of this institute. It would probably be well to avoid the term "composi-

*Paper presented at the annual meeting of the American Institute of Metals, Sept. 7-11, 1914, at Chicago, Ill.

¹First Report of the Committee on the Nomenclature of Alloys. JI. Inst. Metals, 11, p. 45; 1914.

²Zur Einheitlichen internationalen Nomenklatur der Legierungen. W. Guertler, Int. Zs. f. Metallographie, 6, p. 23; 1914.

³Nomenklatur und Normen für Bronzen, v. Moellendorf. Ges. Zs. 11, p. 23; 1914.

⁴Corse and Skillman, Met. & Chem. Engr. 12, p. 113; 1914.

tion" as used by Mr. Karr for systematic names and leave it for use as a convenient expression for an alloy containing three or more components, including always copper, which latter practice is common in America. Thus any alloy of copper, tin and zinc might be called a "composition," but the systematic name of the Zn 2-Sn 10-Cu 88 would be "zinc-bronze" and the alloy with Sn 2-Zn 10-Cu 88 would be "tin-brass," in accordance with the proposed British nomenclature. If now manganese and iron are added to this tin-brass and the manganese contributes markedly to the resulting properties we should call the resulting alloy of composition Mn 0.5-Fe 1.0-Sn 2-Zn 10-Cu 86.5 a manganese "complex" brass in the British notation. German silver may still be called such but it might also be classed as a nickel-brass.

Dr. Guertler, following others, suggests abbreviating the names of the elements making up an alloy and, for binaries, combining these abbreviations into a single word, the preponderating element being named last. Thus he would say "cupral" for copper-aluminum and "alcup" for aluminum-copper. He gives a complete list of prefixes and suffixes.

Regarding the metallographic constituents, Robin⁹ in 1912 suggested the use of an abbreviated rational notation based on the use of letters designating solutions, eutectics, etc. Guertler proposes to follow the practice in vogue for iron and use the suffix "it" (or "ite" in English) for elementary crystals of metallographic constituents, giving with "ferrite," such terms as "Platite," "Cuprite," etc., and Al-Cuprite for the solid solution of Aluminum in Copper, etc. The Greek letters, according to him, should be left for the several phases of the elements as α , β , γ , δ iron, α β copper, etc., and a new system of symbols devised for the intermediate crystal phases in an alloy, such as the letters P, Q, S, U, Z. Guertler would also use the expression "bronzite" to indicate in the bronzes the structure corresponding to "pearlite" in the ferrous nomenclature.

This Institute is primarily interested in the first aspect of the nomenclature question, i. e., the naming of the alloys. In view of the conservative nature, reasonableness and practical simplicity of the principles advocated in the Report of the British Committee, and for the sake of uniformity of usage, which is most desirable of attainment, it would appear advisable for this Institute to adopt the British suggestions on non-ferrous nomenclature.

It would also appear worth while for the Advisory Committee to the Bureau of Standards on non-ferrous alloys to continue the consideration of this subject. There are several questions related to nomenclature which have not yet received sufficient attention, such as tolerances for allowable limits of components in definitions of different classes of alloys; tolerances

as to impurities allowable without modifying the name; and standard specifications for the several classes of alloys and suitable tests for their fulfillment; all of which, and many related questions, are of the greatest practical importance and for the solution of which the available data are as yet for the most part all too meagre.

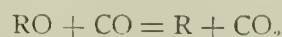
SPELTER—MANUFACTURE AND PROPERTIES.*

By GEORGE C. STONE.

The chemical properties of zinc are unique and render its extraction from an ore impossible by the methods used for the other common metals. The temperature at which oxide of zinc is reduced by carbon is considerably higher than the volatilizing point of the metal, so that it is always produced as a vapor. In order to obtain the metal in a commercially useful form it must be condensed at a temperature above its melting point, because if suddenly cooled to a solid it condenses as a powder, which oxidizes very readily and cannot be remelted and cast to form a solid. In ordinary metallurgical practice the oxide of a metal is heated with carbon or in an atmosphere of CO, either of which reduces the oxide to metal under the conditions which are maintained in the furnace. The reaction is



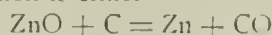
or



The furnace atmosphere is essentially a mixture of nitrogen, carbon dioxide and carbon monoxide, and for all metals but zinc the presence of a considerable amount of carbon dioxide is not harmful. For zinc the case is different, as the presence of even a fraction of a per cent of carbon dioxide causes the action to reverse, and we have



It is therefore necessary always to have an excess of carbon present in order to produce metallic zinc, and the reaction is either



or



These reactions were not known, and zinc as a metal by itself was not known, until early in the nineteenth century. Zinc as a constituent of brass was known for centuries before this. The old method of making brass was to heat the zinc ore with copper and charcoal. The zinc was reduced by the carbon and immediately alloyed with the copper and was thereby prevented from volatilizing completely, as it would if the copper were not present. The percentage of zinc in the resulting brass was naturally very uncertain and the quality of the product varied greatly. I have, myself, made brass in this way, maintaining as uniform

⁹Nomenclature of the non-ferrous Alloys. C. P. Karr, Trans. Am. Inst. Metals, 7, p. 147; 1913.

¹⁰Utility of a Metallographic Nomenclature, Felix Robin, Int. Ass. Test. Mats. 1, 11 8; 1912.

*Paper presented at the annual meeting of the American Institute of Metals, Sept. 7-11, 1914, at Chicago, Ill.

conditions as possible, and the brass from the different runs contained from 8 per cent to 25 per cent of zinc.

There are two main classes of ores, the sulphides, blende, and the oxidized ores, carbonates and silicates. The sulphides must be roasted to oxides before smelting. The oxidized ores require no preliminary treatment. Blende is the most abundant ore of zinc and is mined in Virginia, Kentucky, Tennessee, Missouri, Wisconsin and all of the Rocky Mountain states. It is usually associated with galena (sulphide of lead) and pyrite (sulphide of iron), and therefore usually requires mechanical concentration to separate it from these minerals.

The oxidized ores are found in the same localities as blende, and also in New Jersey, which contains the largest deposits of oxidized zinc ores in the world at Franklin Furnace. In most cases oxidized ores are associated with lead, which is removed as completely as possible by mechanical concentration.

All zinc ores contain iron, usually in considerable quantities. Most of them also contain cadmium in much smaller quantity. The effect of these impurities will be discussed later.

The peculiar chemical properties of zinc limit the possible types of furnace to be employed, and, as a matter of fact, all of the successful zinc furnaces have been of the same general type.

A spelter furnace consists of a chamber with a solid roof and solid walls on three sides. The fourth side is an open frame of firebrick. Retorts closed at one end are placed in this chamber, resting on the open front frame and on projections from the opposite wall. The open ends of the retorts project slightly from the furnace, and the space around them is luted tightly with clay or a mixture of clay and coal. The furnaces are heated either by direct fires or by gas. When the furnace is sufficiently hot the charges consisting of a mixture of crushed ore and coal, is thrown into the retorts with considerable force so as to pack it tightly. A small rod is then pushed through the charge near the top of the retort to make a vent for the gases formed. This operation is called spiesing in the East.

The condensers, short clay cones, are then fitted into the open ends of the retorts and luted with coal. The large ends of the condensers are placed in the retorts and the outer ends are supported on pieces of brick resting on the shelves in front of the furnace, or on movable iron rests called grasshoppers.

The mouths of the condensers are partly stopped with coal to prevent the entrance of air and loss of heat. The heat in the furnace is gradually increased and the condensers watched to make sure they do not get stopped up, which would result in an explosion of the gas confined in the retort. The gas at the end of the condenser is lighted and burns at first with a clear red, yellow or blue flame. In a short time this becomes smoky and tinged with green, showing that the zinc is beginning to come off.

In about six or eight hours enough zinc has been distilled to make it necessary to draw it. This is done by scraping the liquid zinc and oxide in each condenser into a ladle held below it. When the ladle is full the oxide is skimmed off and the metal poured into molds. The operation of drawing requires considerable skill, as all of the material in the condenser should be removed quickly and none of the charge from the retort dragged with it. It is also important that none of the metal in the condenser should be pushed back into the retort, as, if it is, it will immediately be volatilized, burn and be lost.

As soon as the condensers are drawn a helper again stops their mouths with coal. The heat is gradually increased, and in another six hours or so a second draw is made. After the second draw the heat is increased as much as possible and maintained to the end of the charge. When the charge is worked off a third draw is made, the condensers being cleaned as thoroughly as possible. The condensers are then taken out and the material in the retorts removed either by scrapers or by blowing out with steam or water.

The latter operation sounds rather barbarous, but is not as bad as it sounds. It is performed by pushing a pipe through the material in the retort to the back end and turning on steam or water for an instant. If water is used it is immediately converted into steam and acts like an explosion, blowing the material out of the retort. When steam is used, it is usually very wet, owing to condensation in the long pipes necessary.

Any used up retorts are then removed and replaced by new ones, which are brought red hot from the kilns, which should be close to the furnaces. The furnace is then recharged and the operation goes on as before. It requires twenty-four hours to work off a charge.

The ladle skimmings, condenser scrapings, chips from old retorts, and any metal spilled, are carefully collected and added to the next charge.

The success of the operation depends on the proper mixing and proportioning of the charge, the regulation of the heat, and the care and skill of the workmen.

Up to twenty years ago the furnaces were very small and were all fired directly with coal. A furnace crew then consisted of a charger and a long-shaft man, both of whom worked twenty-four hours, and a short-shift man who worked twelve hours. They wheeled and mixed the charge, fired and worked the furnace, drew the metal, replaced retorts, and took the metal made to the storehouse. The charger was responsible for the firing of the furnace, and the success or failure of the work depended almost entirely on him. It was never easy to get sufficiently intelligent, careful and skillful men who were willing to work twenty-four hour shifts, and it became increasingly difficult to do so as other lines of employment opened. The endeavors of the managers have therefore been to de-

sign furnaces and plants that do not depend so entirely on the skill of the workmen. In this they have been largely successful. The charges are now usually mixed by machinery, concrete mixers being frequently used. The furnaces are fired by gas, giving easy regulation. The spelter was formerly drawn off in hand-ladles holding about forty pounds each. These had to be moved by hand from retort to retort, lifted up and down and carried to the molds. While doing this work the men had to stand close to the furnace with no protection from the heat. At the present time much larger ladles holding from 200 to 500 pounds are used. They are carried on cranes on cars provided with shields to protect the men from the heat of the furnace. When the ladle is full the car is run to the molds and the metal poured, the ladle being still carried on the crane, by which its height can be adjusted for convenient pouring.

The ventilation of many of the old spelter furnace buildings was very defective and they were frequently full of smoke and gas. In strong winds this was particularly troublesome, as it was necessary to close all openings on the windward side of the buildings because drafts interfere with the working of a furnace. At the present time the furnaces are usually built with very large hoods and clear openings over them so that the ventilation of the rooms is practically perfect. At some works an air pipe is run near the roof and parallel to the front of the furnace with open branches pointing toward the floor at a point about 2 ft. back of the position of the men when working at the furnace. By moving back one step the men can get the cool draft and do not have to stay in it long enough to get chilled. This has proved of great advantage in hot weather. The general health of spelter men is excellent and no occupational diseases due to zinc are known. In a few cases where ores high in lead are worked authentic cases of lead-poisoning have occurred. The so-called "spelter shakes" are unknown in zinc works, and this trouble is certainly due to something other than zinc.

The work is so arranged that no men work more than twelve hours, and most of them only about six. The largest number are required when cleaning out and charging. As soon as this is completed all but the metal drawers are free to go home. It is still hard, hot, dirty work, and the hours are inconvenient, as the cleaning out usually starts at 4 or 5 a. m. The men prefer this early start as it is the coolest hour in summer, when the work is most trying.

There are several kinds of furnace in use—the old direct-fired furnace with the fireplace below the retorts has practically disappeared in this country. None is now in operation, and those still in existence will probably never be started up again. The simplest of the gas furnaces is the Hegeler, invented by Mr. Edward C. Hegeler, one of the pioneers in zinc smelting in this country and one who has probably done more than anyone else to improve the practice.

The Hegeler furnaces are very large, some containing as many as 1,080 retorts. The gas is all admitted at one end, the producer being placed close to the furnace so as to utilize as much as possible of the sensible heat. The air is admitted at different points lengthwise of the furnace so as to burn the gas gradually.

The furnaces used in the natural gas field are similar except that both gas and air are taken in at intervals along the front. This type of furnace is cheap to build and easy to operate, but is not economical in fuel. To Mr. Hegeler this made no difference as he had very cheap fuel and means for utilizing all of the waste heat.

Various modifications of the Siemens furnace are largely used. In these the retorts are faced two ways, the butts of all resting on projections from the center wall, which does not come quite up to the roof. There are four regenerators under the furnace, and the gas and air coming from two of these enter ports under the lowest row on one side and pass over the center wall through ports below the retorts on the opposite side to the other pair of regenerators. At regular intervals, usually of about half an hour, the gas and air are reversed in direction. In this way the retorts are kept at a fairly uniform temperature. This type of furnace is very economical in fuel, but requires considerable care and judgment to get and maintain a uniform distribution of heat. It is impossible to keep the regenerators clean, and they gradually lose their efficiency.

The Convers de Saulles furnaces are used by only one company. In these the gas is taken hot from the producers and the air is heated in continuous regenerators. Both air and gas enter both sides of the furnace under the lowest retorts and pass out through the hollow back wall. As the air alone is regenerated this furnace is not as economical as the Siemens, but is much easier to operate. The regenerators are built with straight passes that can be kept clean so that the efficiency of the furnace can be maintained until the brick work of the chamber gives way.

In Europe several other furnaces have been used with considerable success, but none of them have proved satisfactory when tried in this country.

A very important accessory operation is the manufacture of retorts. Formerly they were made entirely by hand, which was slow and required a skilled potter. At the present time they are made in tile machines, or more often in hydraulic presses. The latter makes much denser retorts than either of the other processes, and they can be made with much thinner walls and are therefore easier to heat. After pressing, the retorts are placed in drying rooms where they are kept for three months or longer. Each morning the potterly man finds out from the furnace men how many retorts will be required the next day, and places the proper number in the kilns where they are burned with coal or gas for about eighteen hours. The kilns are close

to the spelter furnaces and the retorts are transferred while red hot.

IMPURITIES IN SPELTER.

The commonest impurities in spelter are lead, iron and cadmium. Arsenic is also quite common, but very little attention is paid to it. All of these impurities are derived from the ore and will be found in the spelter if they occur in the ore. In other words, it is impossible to make pure spelter from impure ore. The extent to which the different impurities in the ore go to the spelter varies considerably.

When lead is present in the ore in very small proportion (about one of lead to a thousand of zinc), practically all of it will be found in the spelter. As the proportion of lead to zinc in the ore increases the proportion of the total lead that goes to the spelter decreases. It is difficult to make a spelter containing much over 2 per cent of lead, no matter how much the ore contains. Lead and zinc make fairly homogeneous alloys up to about 1 per cent of lead. When more is present it segregates badly.

Iron behaves quite differently, and the amount of it found in the spelter depends mainly upon the way the smelting is conducted and not on the amount in the ore. It is possible to make spelter as free from iron from ore that contains 10 or 12 per cent as from ore that contains 1 to 2 per cent. The two causes that mainly contribute to the presence of iron in the spelter are careless drawing, by which part of the charge is drawn into the condensers and poor scrapers which wear off and introduce particles of iron.

Cadmium is much more volatile than zinc and a good deal of that contained in the ore escapes condensation so that the spelter never contains as much cadmium as the composition of the ore would lead us to expect.

The behavior of arsenic has not been much studied, but we know that it is found in the spelter whenever it occurs in the ore.

Aluminum and tin are never found in virgin spelter, that is, spelter made from ore. Tin never occurs with zinc, and aluminum is not reduced under the conditions occurring in a spelter furnace.

Commercial spelter is divided into four grades, which have been defined as follows by the American Society for Testing Materials:

- (a) High Grade. Shall not contain over
0.07% lead
0.03% iron
0.05% cadmium

It shall be free from aluminum.

The sum of the lead, iron and cadmium shall not exceed 0.10%.

- (b) Intermediate. Shall not contain over
0.20% lead
0.03% iron
0.50% cadmium

It shall be free from aluminum.

The sum of lead, iron and cadmium shall not exceed 0.50%.

- (c) Brass Special. Shall not contain over
0.75% lead
0.04% iron
0.75% cadmium

It shall be free from aluminum.

The sum of the lead, iron and cadmium shall not exceed 1.2%.

- (d) Prime Western. Shall not contain over
1.50% lead
0.08% iron

The following table gives the analyses of typical samples of the various grades:

HIGH GRADE		
Pb	Fe	Cd
.010	.026	0.04
.041	.014	None
.035	.014	"
INTERMEDIATE.		
.095	.009	None
.190	.017	"
.123	.011	0.12
BRASS SPECIAL.		
.343	.026	None
.474	.013	"
.680	.010	0.274
PRIME WESTERN.		
.87	.062	.023
.644	.013	1.09
1.27	.011	.079

STRENGTH OF SPELTER.

Spelter is a highly crystalline metal and its tensile and transverse strength depend entirely on the size of the crystals. The tensile strength varies from about 2 tons per sq. in. with coarsely crystalline specimens, to 7 tons with very fine grained ones. The composition does not appear to influence the strength greatly.

The transverse strength also varies with the crystallization, being greater the finer the grain. The modulus of rupture varies from 4 to 11 tons per sq. in. with deflections of from 0.09 to 0.44 in. on a span of 12 in. There is no definite relation between the modulus of rupture and deflection. The purer the spelter the higher the deflection it will stand without cracking.

The compression test pieces were cylinders 1 in. in diameters and 2.6 in. long. The load necessary to compress these at 10 per cent and 20 per cent was determined:

Names	10%	20%
High Grade	16,500	23,095
Intermediate	16,065	23,095
Brass Special	18,310	26,000
Prime Western	20,570	28,620

The resistance to compression increases with increase of impurities. The effect of the different impurities varies greatly. Lead has but little influence. Iron has comparatively little influence. Cadmium increases the resistance to compression very greatly. A cadmium-free Brass Special spelter required 17,190 lbs. to compress it 10 per cent, while a Prime Western spelter with 0.32 per cent cadmium and about the same quantities of lead and iron as the other required 27,340 lbs. In another case a cadmium-free metal required 16,500 lbs. for 10 per cent compression, while the same

metal to which .2 per cent of cadmium had been added required 26,870 lbs. For 20 per cent compression the cadmium-free required 24,000 lbs. and the metal with .2 per cent cadmium 37,000.

EFFECTS OF IMPURITIES.

Lead: Lead in moderate quantity tends to make spelter softer in rolling; in galvanizing it has a tendency to weaken the coating and make it more liable to peel when the coated metal is bent. Present in quantities about .7 per cent it tends to produce bad cracking in spelter castings. In brass it tends to make the alloy more brittle and liable to crack.

Iron: Iron hardens spelter and makes it more brittle. This effect seems to follow through all of its uses. In galvanizing excessive iron also tends to make more dross, the iron being present in the form of a solid alloy, gradually settles to the bottom of the pot; though this effect is slight, as much more iron is added to the bath by the containing vessel and the material being galvanized than can possibly be present in the spelter.

Cadmium: The effect of cadmium is to harden spelter greatly and make it more brittle. In galvanizing this is very important as the brittleness due to the cadmium causes the coating to peel off. This is of particular importance in telephone and telegraph wires which are sharply bent in making splices. If the zinc contains appreciable quantities of cadmium the coating peels off at these points and the life of the line is much shortened. Cadmium has a strong tendency to make castings crack. It also makes the metal less fluid and its presence makes it impossible to make as light slush castings. In brass cadmium tends to act like lead and is also said to make the metal more sensitive to heat treatment. Luckily for the brass makers a large part of the cadmium in the spelter they use is volatilized and lost so that the amount in the resulting brass is rarely large enough to cause much trouble.

Arsenic: In the ordinary uses of spelter, arsenic in the quantity in which it occurs does not appear to have much effect. When used for generating hydrogen to be used in lead burning, it does, however, have a very important influence, making it impossible to burn a strong seam.

In general the purest spelter gives the best results, and very pure spelter can only be made from pure ores. There are several refining processes which reduce the amounts of some of the impurities and have little effect on others. In Europe it is customary to remelt all of the lower grade spelter corresponding to our Prime Western. This is done in large reverberatory furnaces holding as much as 15 or 20 tons of spelter, which are heated to a temperature just sufficient to keep the metal liquid. A considerable part of the lead and some of the iron settles to the bottom of the furnace, and the purer zinc is ladled from the top and cast for sale. The lead is reduced to about 1 per cent and the iron to about 0.03 per cent. Cadmium is very little affected, as it dissolves in the zinc in amount up to 1 per cent and, therefore, cannot be sep-

arated by liquation. The main advantage is not so much in the reduction of the amount of impurities as in the production of a more uniform grade of metal.

In this country the so-called refining is usually the treatment of scrap and galvanizers refuse in the production of what the Government calls secondary zinc. The product made is of uncertain quality and usually contains impurities, notably tin and aluminum, not found in spelter made direct from ore. While some of this material shows a fairly good chemical composition, it is usually hard and brittle due to excessive cadmium, and will not produce the results for galvanizing, alloys or castings that can be obtained from good virgin spelter.

The final jute crop forecast issued by the Indian Government gives a grand total acreage of 3,358,737, as compared with 2,910,960 acres in the previous year. These figures have been exceeded only in the season of 1907-8, when the final acreage returns gave 3,883,200, yielding 9,817,100 bales of jute, whereas the yield for the present year is now estimated at 10,531,505 bales of 400 pounds each. This estimated outturn shows an increase of over 1,500,000 as compared with 1913.

The total production of platinum from California and Oregon in 1913, according to the U. S. Geological Survey, amounted to 482.87 crude ounces and was valued at \$18,477. Of this, 460.37 crude ounces came from California and were rated at 80 per cent fine—that is, it contained 368.3 fine ounces of platinum. That from Oregon—22.5 ounces—was not so carefully cleaned and was reckoned at 70 per cent fine, or 15.75 fine ounces of platinum. The greater part of the California platinum came, as usual, from the large gold-dredging operations in Butte, Yuba, Sacramento, and Calaveras Counties. The production of refined platinum in the United States from domestic sources in 1913 was 1,034 troy ounces, valued at \$46,530. The question of a larger yield of domestic platinum depends principally upon working the Oregon and California beaches, including the old beaches now several miles inland and elevated considerably above sea level. Several machines involving somewhat fanciful or novel ideas were installed during 1913. As a rule, these machines were handicapped because they consisted either of competent concentrating apparatus without adequate means for digging the crude sand and delivering it to the concentrator, or, in other places, the reverse has been the case, and the machine, well suited for large-scale excavation at a low cost, has not been equipped with a proper system for concentrating these heavy sands after excavating them.

If more platinum were greatly needed, the supply could be augmented from California and Oregon.

During August, 1914, exportation of nitrate of soda through the customhouse at Iquique, Chile, was 27,100,669 quintals.



METHODS OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR INSTITUTE OF TECHNOLOGY.

Analysis of Vinegar.

INTRODUCTORY.

The principal vinegars on the market today, are as follows: Cider vinegar, "White wine" spirit, distilled, or grain vinegar, malt vinegar, molasses or "black strap" vinegar, wine vinegar, white and the red.

Other vinegars sold are the terragon malt, celery, etc.—brands of the above that are flavored with extracts of plant life—and fermented fruit juices from strawberries, gooseberries, raspberries, peaches, etc.

Cider vinegar is made from apples that are wind-falls, specked, gnarled and poorly shaped, or otherwise unfit for table use. The juice is expressed by big presses and fermented in large tanks of many thousands of gallons capacity. The alcoholic liquor, containing many soluble and some insoluble substances, is then run through generators—tanks filled with beechwood shavings—where it is oxidized by the air sucked through the generators, to acetic acid. This acetic acid mixed, of course, with a large volume of H_2O contains many soluble and some insoluble ingredients which make up the ash and solids.

Many cider plants use but the skin and cores for the making of cider vinegar and use the meat of the apple for canning or dried fruit purposes.

The "white wine" spirit, distilled, or grain vinegar is made from a fermented grain mash. Corn and rye, or corn, rye and malt, are cooked, mixed, and pitched with a race of yeast producing a high alcohol yield. This alcoholic mash is then emptied into a distil. The distillate is mixed with vinegar and run through generators. This distilled vinegar is a clear, pure, colorless product containing practically no ash or solids. Black strap, or molasses vinegar, is now also used for distilled vinegar. The molasses is fermented and distilled and then generated.

Malt vinegar is made similar to a beer mash with the exception that an effort is made to produce an extract as rich as possible in sugar (maltose) but poor in dextrine. Malt is rarely used alone, but as the basis. Barley, oats, sugar or syrup are used with malt. This vinegar contains considerable quantities of nitrogenous matter, and it runs high in phosphates, dextrine and maltose. It has high solids and ash. After the fermentation is completed the liquor is generated and the vinegar is then aged several years.

Molasses or "black strap" vinegar, often called

sugar vinegar, is made from the molasses refuse of sugar refineries. The molasses is diluted with water, cooked, cobbled, and fermented in large vats. If the finished product is to be sold as sugar vinegar it is clarified with bone dust and generated. If it is to be sold as spirit vinegar, it is, after fermentation, distilled.

This vinegar, as sugar vinegar, has the color of cider vinegar and is very often sold as an illegal substitute for it. There are practically no solids, but its ash runs high.

Grape or wine vinegar is made from the juice expressed from grapes fermented and then generated. However, grapes are generally too high priced for vinegar purposes so, therefore, a large share of the wine vinegar is made from spoiled wine. The spoilage generally consists of acetic acid ferment and impairs the flavor of the wine for drinking purposes. This spoiled article is run over generators and the alcoholic liquor converted to acetic acid. This vinegar contains, as does the malt and cider vinegar, high solids and considerable ash.

VINEGAR ANALYSIS.

Specific Gravity—Take with hydrometer at 15.6° C. Westphal balance or pycnometer may also be used. The specific gravity is a rough check on the solids and on the alcohol.

Acidity—6 cc. of vinegar are carefully measured from a pipette into a white porcelain dish and diluted with water. Using phenolphthalein as an indicator, titrate with tenth normal sodium hydroxide. The number of cubic centimeters of the latter required to neutralize, divided by 10, expresses the acidity in terms of percentage of acetic acid. Vinegar is bought and sold according to its strength expressed by the trade in grains. One per cent strength acetic acid equals 10 grains.

Alcohol—Make 100 cc. faintly alkaline with strong NaOH, distil 50 cc., filter if not clear, and take specific gravity at 15.6° C. Calculate the percentage by weight from a table. Table II, page 103 of Bull. 107 issued by the United States Government, is desirable. This determination gives the completeness of the acetification.

Total Solids—Evaporate 10 cc. in a flat bottom 50 mm. weighed platinum dish to a thick syrup. Heat at 100° C. for $2\frac{1}{2}$ hours. Weigh.

Ash—Char 25 cc., moisten, dry, and reheat at low redness until white or nearly white ash is obtained.

Solubility and Alkalinity of Ash—Extract the ash three times with 10 or 15 cc. of boiling water, filter on

a weighed gooch. Wash repeatedly with hot water, ignite and weigh as insoluble ash. Soluble ash is calculated by difference. The filtrate is cooled and titrated with HCl or H_2SO_4 , using methyl orange.

Phosphoric Acid of the Ash—Determine in soluble and insoluble portions of the ash. Extract the insoluble ash obtained as above directed repeatedly with hot water acidulated with nitric acid. Acidify with nitric acid the neutralized solution of the soluble ash. Add 15 gms. of ammonium nitrate to each solution and heat to boiling. Precipitate the phosphoric acid with 50 cc. of ammonium molybdate. Digest about an hour at a temperature of 65°C ., filter and wash with cold water. Dissolve precipitate on the filter with ammonia and hot water and wash into a beaker to a bulk of not more than 100 cc. Nearly neutralize with HCl and add magnesia mixture drop by drop and stir vigorously. After fifteen minutes add 30 cc. of ammonia. (Sp. gr. 96), let stand for at least two hours, filter on a gooch crucible, wash with 2.5 per cent ammonia till practically free from chlorides, ignite and weigh as $\text{Mg}_2\text{P}_2\text{O}_7$.

Fixed Acids—Evaporate 10 cc. to dryness in a large evaporating dish, add 5 cc. of water and evaporate again. Add successive portions of 5 cc. of water four and five times and evaporate until free from acetic odor. Dilute to 200 cc. with boiled distilled water and titrate with N/10 alkali, using phenolphthalein.

Polarization—To 50 cc. vinegar add 5 cc. lead subacetate (10 per cent strength), shake and let stand 30 minutes. Filter and polarize at 20°C . Reading obtained is the direct reading or polarization before inversion. The polarization is conveniently expressed in terms of actual direct reading obtained by the undiluted sample in a 200 or 400 mm. tube, Ventzke scale.

Reducing matters before inversion—Take 25 cc. each of copper and alkaline tartrate solutions and 10 cc. of vinegar and dilute to about 100 cc. in a 400 cc. beaker. Cover and heat so as to boil in four minutes and boil two minutes. Filter, wash with water at 60°C ., then with 10 cc. of alcohol and then 10 cc. of ether. Dry at 100°C . thirty minutes and weigh. Calculate as invert sugar using table on page 243, Bull. 107.

Reducing sugar—Evaporate 50 cc. to 5 cc. Twice add 25 cc. water and evaporate to 5 cc. Dilute to 100 cc., mark and determine as above using 20 cc. aliquot diluted to 50 cc.

Reducing sugar after inversion: Invert 40 cc. of the above solution, after diluting to 75 cc. by adding 5 cc. of HCl and subjecting to 70° for 10 minutes and cooling. Neutralize with Na_2CO_3 and make up to volume of 100 cc. Determine reducing sugar as above using 50 cc. aliquot.

Malic Acid—If no precipitate occurs with a few drops of neutral acetate of lead in an analysis of a cider vinegar, then the vinegar may be condemned immediately as an illegal cider vinegar. The precipitate should form at once, if flocculent, and should settle to the bottom of the liquid within ten minutes.

However, other organic acids will give a precipitate such as malic will—tartaric and succinic acids. The former occurs in wine while the latter occurs in molasses vinegar. Malt vinegar also gives a precipitate with lead acetate due to the phosphoric acid.

Add a few drops of a 10 per cent solution of calcium chloride to some of the vinegar in a test tube and make contents slightly alkaline with ammonia. Filter off the precipitate, and to filtrate, add two or three volumes of 95 per cent alcohol and heat to boiling. A flocculent precipitate of calcium malate will form if malic acid be present, settling to the bottom in a few minutes. A precipitate will also occur in malt and glucose vinegar due to dextrine.

To confirm malic acid, filter, wash the precipitate, dissolve it in strong nitric acid in a porcelain evaporating dish and evaporate to dryness over water-bath, forming calcium oxalate. Boil the residue with sodium carbonate, filter, acidify the filtrate with acetic acid, boil to expel the carbon dioxide, and add a solution of calcium sulphate. A precipitate of calcium oxalate confirms the presence of malic acid.

Determination of Free and Combined Malic Acid in Cider and Wine Vinegars—Evaporate 100 cc. of sample on water-bath to half its volume, cool, and treat first with 10 cc. of 10 per cent calcium chloride solution and then with ammonia to strong alkaline reaction. Let stand an hour and filter to remove tartaric acid. Concentrate filtrate on water bath to about 25 cc., and 75 cc. of 95 per cent alcohol, heat to the boiling point and filter. Wash residue with a mixture of three parts 95 per cent alcohol and one part water, dry, and burn to ash. Add 25 cc. N/10 HCl to the ash, dilute with water, heat to boiling, and titrate with N/10 NaOH, using phenolphthalein as an indicator. Multiply the difference between 25 and the number of cc. required to neutralize by .0067 for gms. of malic acid.

Determination of Acid Tartrate of Potassium in Wine Vinegar—Berthelot and Fleuricus Method—25 cc. of the vinegar are evaporated on the water bath to a syrupy consistency and the residue is dissolved in water and made up to its original volume. It is then transferred to a 250 cc. Erlenmeyer flask and 100 cc. of a mixture of equal parts of strong alcohol and ether are added, the flask is corked, shaken and set on ice or in a cold place for 48 hours. At the end of that time, if a crystalline precipitate has gathered, the supernatant liquid is decanted upon a filter and finally the precipitate is washed upon it by a fresh quantity of the ether-alcohol mixtures and the washing continued with this reagent till practically free from acid. The filter and its contents are then transferred to the original flask and the tartrate is dissolved in boiling water, after which the solution is titrated in the same flask with tenth normal sodium hydroxide, using phenolphthalein as an indicator. Multiply the number of cubic centimeters of alkali to neutralize by the factor

.0188 and the quotient expresses the grams of bitartrate of potash in the sample.

Nitrogen in Malt Vinegar—Concentrate 50 to 100 cc. of vinegar to syrupy consistency and nitrogen is determined by the Kjeldahl or Gunning method.

Detection of Caramel—Test Modified by Laschi—Add 10 cc. of paraldehyde to 5 cc. of the sample contained in a test tube and shake. Add absolute alcohol, a few drops at a time, shaking after each addition until mixture becomes clear. Allow to stand. Turbidity after 10 minutes is an indication of caramel.

Detection of Free Mineral Acid—Frcar's Method—Add 5 to 10 cc. of water to 5 cc. of the vinegar, and to the mixture add a few drops of a solution of methyl violet (one part of methyl 2B in 100,000 parts of water). In presence of mineral acids a blue or green coloration will be produced.

Determination of Free Mineral Acids—Hehner's Method—To a weighed quantity of the sample add an excess of decinormal alkali, evaporate to dryness, incinerate and titrate the ash with decinormal acid. The difference between the number of cc. of alkali added in the first place, and the number of cc. needed to titrate the ash, represents the equivalent of free acid present.

Detection and Determination of Sulphuric Acid—According to Brann, if the quantity of sulphuric acid is more than one part in a thousand, the sulphate of barium formed by the addition of barium chloride produces a copious precipitate that rapidly falls to the bottom of the receptacle. A slight turbidity indicates presence of sulphuric acid as an impurity and not as an added product. The precipitate from a measured quantity of vinegar is filtered, washed, ignited, and weighed in the usual manner.

Detection of Free Hydrochloric Acid—Distill off half of a measured volume of vinegar into the receiving flask of a distillation apparatus, and to the distillate add a few drops of nitrate of silver reagent. A precipitate indicates hydrochloric acid.

Glycerine Determination—All evaporations are made on a water bath, the temperature of which is maintained at 85 to 90°.

Evaporate 100 cc. of vinegar to 5 cc., add 20 cc. water and again evaporate to 5 cc. in order to expel acetic acid. Treat the residue with about 5 gm. of fine sand and with 15 cc. of milk of lime containing the equivalent of 15 per cent CaO, and evaporate almost to dryness with frequent stirring, avoiding formation of a dry crust or evaporation to complete dryness. Treat the moist residue with 5 cc. water, rub into a homogeneous paste and then add slowly 45 cc. of absolute alcohol, washing down the sides of the dish to remove the adhering paste, and stir thoroughly. Heat the mixture on a water bath, with constant stirring, to incipient boiling, and decant the liquor through a 12.5 cm. fluted filter into a porcelain dish. Wash the residue repeatedly with small portions of hot 90 per

cent alcohol, twice in decantation, and then transferring all the material to the filter, continuing the washing until the filtrate amounts to 150 cc. To save time the first 75 cc. of filtrate may be placed on the water bath to evaporate while the second 75 cc. is being collected, the last being then added to the first portion. Evaporate to a syrupy consistency, add 10 cc. absolute alcohol to dissolve this residue, and transfer to a 50 cc. cylinder, washing the dish with successive small portions of absolute alcohol until the volume of the solution amounts to 20 cc. Then add 3 portions of 10 cc. each of absolute ether, thoroughly shake after each addition. Let stand until clear, then pour off through a filter and wash the cylinder and filter with a mixture of two parts of absolute alcohol and 3 parts of absolute ether. If a heavy precipitate has formed in the cylinder it is advisable to centrifuge at low speed, decant the clear liquid, add 20 cc. of the mixture of absolute alcohol and absolute ether for washing, shaking and again centrifuge, repeating this process three times. Wash the paper with the alcohol-ether mixture, and evaporate the filtrate and washing to about 5 cc. on the water bath, add 20 cc. water, evaporate to 5 cc.; again add 20 cc. water and evaporate to 5 cc.; finally 10 cc. of water and evaporate to 5 cc. (these evaporations being necessary to remove all the ether and alcohol, and when conducted at 85-90° resulted in no loss of glycerine if the concentration of the latter is less than 50 per cent). Transfer the residue with hot water to a 50 cc. graduate flask, cool, add silver oxide freshly precipitated from 0.1 gram of silver sulphate, shake and allow to stand 10 minutes; then add 0.5 cc. of lead subacetate solution, shake occasionally and allow to stand 10 minutes; make up to mark, shake well, filter, rejecting the first portion of the filtrate, and introduce 25 cc. of the clear filtrate (measure from a 25 cc. burette) into a 250 cc. volumetric flask. Add 1 cc. of concentrated sulphuric acid to precipitate the excess of lead (which otherwise would subsequently combine with part of the standard bichromate, causing an error) and treat this solution as indicated below for the estimation of glycerine.

Determination of Glycerine by a Modified Hehner's Bichromate Oxidation Method—(a) Solution required.

(1) Strong bichromate: Dissolve 74.615 grams dry, recrystallized potassium bichromate in water, add 150 cc. concentrated sulphuric acid, cool, make up to 1,000 cc. at 20° C. and determine the specific gravity of the solution at 20°/20° C. 1 cc. of this solution equals 0.01 grams glycerine. The high coefficient of expansion of this strong solution makes accurate volumetric measurement difficult on account of the changes in the room temperature from day to day and it is therefore necessary to take the specific gravity and use weighed amounts of the solution, which may be conveniently introduced into the tests by means of a weighed burette. Then the weight of the solution used in a given test divided by the specific gravity equals the volume used.

(2) Dilute bichromate; introduce a weighed amount (12.5 times the specific gravity) of the strong bichromate from a weighed burette into a 250 ccgs. volumetric flask, dilute with water and make up to the mark at room temperature. 20 cc. of this solution is equivalent to 1 cc. of the strong bichromate. If the weight taken is slightly in excess of the 12.5 cc. equivalent, make up to the mark and then add required amount of water to make one twentieth dilution.

(3) Ferrous ammonium sulphate: Dissolve 20 grams of crystallized ferrous ammonium sulphate in water, add 50 cc. of concentrated sulphuric acid, cool and dilute to 1,000 cc. at room temperature. 1 cc. of this solution is approximately equivalent to 1 cc. of the dilute bichromate. Its value changes slightly from day to day and should be standardized against the dilute bichromate whenever used. (b) Oxidation of glycerine.

From a weight burette introduce into the 250 cc. flask, containing the 25 cc. purified glycerine solution, a weighed amount of the strong bichromate solution, sufficient to leave about 12.5 excess (with ordinary wines purified as above use 30-35 cc.) carefully add 24 cc. of concentrated sulphuric acid, rotating flask gently to mix contents and avoid violent ebullition, then place in *boiling* water bath for exactly twenty minutes. Remove flask from bath, dilute, cool, and make up to mark at room temperature.

(c) Titration.

(1) Standardize the ferrous ammonium sulphate so-

lution against the dilute bichromate solution by introducing from the respective burettes, approximately 20 cc. of each of the two solutions into a beaker containing 100 cc. of distilled water. Complete the titration using *potassium ferricyanide* solution as the indicator on a porcelain spot plate. From this titration calculate the volume (f) of ferrous ammonium sulphate equivalent to 20 cc. of the dilute and also, therefore to 1 cc. of the strong bichromate solution.

(2) In place of the dilute bichromate solution, now substitute a burette containing the oxidized glycerine with excess bichromate-solution and ascertain how many cc. of it are equivalent to (f) cc. of the ferrous ammonium sulphate solution and also, therefore, to 1 cc. of the strong bichromate. Then 250 divided by this last equivalent equals the number of cc. excess of the strong bichromate solution present in the 250 cc. flask after oxidation of the glycerine.

(3) The number of cc. strong bichromate added, after the excess found after oxidation, multiplied by 9.01 grams equals the weight of glycerine in the weight cc. of purified solution used in the determination; this result multiplied by the four gives the weight of glycerine in grams per 100 c.c. of the vinegar. The C. P. glycerine used in the work was shown by a careful specific gravity determination to contain 95.25 per cent glycerol. A 1 per cent glycerine solution was made by using 10.4987 grams of this C. P. glycerine per liter. Two direct bichromate determinations on 25 cc. portions of this solution gave 0.9969 and 0.9975 per cent instead of 1.0 per cent.

TABLE I.

Sp. Gr.	Solids.	Character of Solids.	Ash.	Character of Ash.	Polarized Light.
Spirit	1.008	Insignificant.	.08	Very slightly alkaline. Trace of phosphoric acid. No soluble phosphoric acid.	No optical activity.
Vinegar	1.013		.09		
Cider	1.013	Light brown and viscid. Alkaline reaction. Baked apple taste and odor. Very soluble in alcohol. Flame test pale blue of potash.	2.0	Strongly alkaline. High in alkali carbonates. Considerable amt. of phosphoric acid and more than $\frac{1}{2}$ is soluble.	Left handed. If more than .50 right hand, adulteration assumed. If direct polarization is RH and invert is LH sugar house waste or molasses an adulterant. If direct and invert are RH commercial glucose present. If polarization far to left cider jelly used, for solids.
Vinegar	1.016		3.20		
Malt	1.014	Sodium flame predominates. Colored brown and is gummy. Alkaline reaction. Slightly soluble in alcohol. On burning an odor like toasted bread.	.28	Quite alkaline, but not so strongly as cider vinegar ash. Considerable amt. of phosphoric acid.	It is generally Loevo-rotary, but may be slightly dextro-rotary.
Vinegar	1.0213		.51		
Wine	1.013	Sodium flame predominates. Dissolves readily in alcohol excepting granular residue of the cream of tartar.	.15	Only vinegar with bitartrate of potash present.	Slightly Loevo-rotary.
Vinegar	1.0213		.85		
Black strap.....	1.009	Sodium flame predominates. On burning the smell of charred sugar apparent.	.16	Sulphate of Calcium. Sometimes high phosphoric acid.	Decidedly dextro-rotary with polarized light before and after inversion.
or Molasses vinegar.	1.013		.61		

On the wholesale market, vinegar today is selling as follows:

Cider vinegar, 40 grains per gallon.....	\$0.10
Malt vinegar, 40 grains per gallon.....	.15
Grape vinegar, 40 grains per gallon.....	.15
Spirit vinegar, 40 grains per gallon.....	.03½
Molasses vinegar, 40 grains per gallon.....	.05

The relatively high cost of cider, malt and grape vinegars to spirit and molasses vinegars furnishes the incentive to duplicate the former by "doping" the latter.

An entirely artificial cider vinegar made by coloring spirit vinegar with caramel and adding apple jelly—the residue or juice of the apple after subjected to one or two pressings—for the solids is often met with. But also cider and grape vinegar are manufactured with the end in view of pressing to get high solids. Then spirit vinegar is added in bulk up to 50 per cent. If solids and ash are low, exhausted apple pressings—juice—and alkali carbonates like potassium and sodium with a little potassium phosphate are added. Glycerine and sugar are added. Grape and malt vinegars are similarly treated. In vinegars so treated it is difficult to detect their illegality especially so in instances when the spirit vinegar, 35 to 40 per cent is added to 55 to 60 per cent cider vinegar. Molasses vinegar is often used as an illegal substitute. It has the color, and so often deludes a hasty examination especially when ash and solids are added. It is also used to "cut" cider vinegar.

Table I tabulates some of the characteristics of the various properties of the vinegars under discussion.

EXAMINATION OF CHINESE WOOD OIL.*

By E. E. WARE and C. L. SCHUMANN.

SUMMARY.

This paper deals with the development of two methods for the quantitative estimation of the adulteration of Chinese wood oil.

The principle upon which the first method is founded is the formation, in wood oil, of an isomeric glyceride that is insoluble in light petroleum ether. This reaction ordinarily takes place very slowly even in bright sunlight, but it may be accelerated by the addition of any one of a number of materials in small quantity. residue consists of the adulterant and the unaffected glyceride of the wood oil. The weight of the unaffected glyceride may be taken as 7 per cent of the weight of the wood oil present.

The second method depends upon the insolubility in alcohol of the potassium soap of elaeomargaric acid. The precipitate may be filtered out and weighed, after drying in a non-oxidizing atmosphere.

The two methods show a degree of accuracy much better than the existing methods, and permit a fairly rapid estimation of the purity of samples of wood oil.

INTRODUCTION.

The use of Chinese wood oil as a varnish oil, although of fairly recent adoption, except in the Orient, has increased rapidly, until at the present time wood oil has come to be considered the important oil of the varnish industry.

The value of the oil has been said to lie in its ability to form actual combinations with the abietic acid of the rosin with which it is cooked. This statement may be open to question, but the fact remains that varnishes of superior quality can be made from wood oil and rosin when they are properly manipulated.

Most of the Chinese wood oil imported into the United States is gathered in small quantities throughout the rural districts of western China, and after passing through the hands of several native collectors and dealers reaches Hankow, where it is put into the export packages. The American buyer, although reasonably certain that he receives the oil as packed at Hankow, has no assurance that the oil he buys is representative of the oil as pressed from the nut. The wide variations that the varnish maker finds in the oil as he uses it may be due to variations in the nut and in its treatment, or to adulteration by one or more of the various middlemen during its open-basket travel from interior China to the forwarder's warehouse at Hankow.

METHODS OF EXAMINATION.

Numerous methods have been proposed for the determination of the relative purity of wood-oil samples. Polymerization of the oil by heating at a definite temperature for a definite length of time, various modifications of which treatment have been proposed by Bacon, Worstall, Potsdamer, Browne and others,¹ is the method in most general use at the present time. This method seems to have given the most satisfaction, since the analytical constants of wood oil vary within rather wide limits, and this variation does not seem to be accompanied by a corresponding variation in the working qualities of the oil, as judged by its action in the varnish kettle.

However, many buyers prefer to depend upon the analytical constants in passing judgment on wood oil, claiming that the personal equation has too strong an influence on the results obtained by the heat polymerization method. The iodine number and the refractive index² seem to be the most reliable constants to use.

McIlhiney³ offers a method for the examination of this oil that promises well when standardized. He precipitates the insoluble iodine addition products formed when wood oil is treated with iodine in acetic acid solution and weighs the oil remaining after evaporation of the solvent from the filtrate.

LIGHT BREAK.

A familiar characteristic that seems to have been neglected in the consideration of methods for judging the purity of wood-oil samples is the light "break." It

*Paper presented at 17th annual meeting of American Society for Testing Materials.

¹Boughton, "Testing of Chinese Wood Oil," Proceedings, Am. Soc. Test. Mats., Vol. XIII, p. 923 (1913).

is a well-known fact that wood oil exposed to the light in bulk soon exhibits a flocculent white precipitate, which continually increases in amount, until after some months the oil seems to be a solid white mass. This change in wood oil upon exposure to light is reported by Normann⁴ to be a polymerization. Fahrion⁵ does not agree with this view, but calls the change a molecular transformation. Normann also finds that light has a similar effect upon the potash soap of Chinese wood oil and that the transformation takes place more rapidly than with the oil.

This break caused by sunlight seems to be characteristic of wood oil alone, and seems to be capable of standardization to the point that permits its use as an analytical method for the estimation of the purity of wood-oil samples.

The authors in studying this phenomenon have made use of certain catalytic agents that markedly influence the rate of transformation. Among these are iodine, sulfur,⁶ hydriodic acid, sulfur chloride, carbon dioxide, hydrogen sulfide, phosphorus tribromide and carbon bisulfide.⁷ These agents act at different rates and bring to completion in times varying from a few hours to several weeks, a reaction that Morrell⁸ reports as proceeding only to the extent of 6 per cent in one year. Sulfur chloride and iodine are the only accelerators studied that will cause a complete precipitation within the time that permits the operation to be classed as an analytical method. Others of the catalyzers might be used as a means of getting a less contaminated product for the examination of its characteristics.

The action of the sulfur chloride upon the drying and semi-drying oils is common knowledge. Jenkins⁹ reports the fact that sulfur chloride added to wood oil to the extent of 20 per cent will yield a jelly-like mass. The reaction is accompanied by an evolution of hydrochloric acid and considerable heat. Chinese wood oil is not alone in exhibiting this characteristic, some of the semi-drying oils showing quite as energetic an action toward sulfur chloride. The fact that such compounds are formed may not therefore be accepted as a test for the purity of wood oil. Gardner¹⁰ suggests that, as Chinese wood oil in carbon-tetrachloride solution will form this addition product much more rapidly than with other oils under the same conditions, the action might be susceptible to a time standardization.

If the wood oil be thinned with a solvent upon which the sulfur chloride will not act, and the dilution be to a strength of solution of 20 per cent or less, the sulfur chloride then becomes merely a catalytic agent for the transformation of the wood oil by light, and there seems to be very little, if any, addition product

formed. The oil will break to a considerable extent even in the dark, but the reaction is very much more rapid if exposed to light. If the concentration of the sulfur chloride be low and the mass cool, the reaction will proceed, until within a few hours the oil is of the consistency of lard. In order that the reaction proceed to completion it is necessary that the break be filtered out at intervals.

The reaction between Chinese wood oil and iodine has been used as a qualitative,¹¹ and the modification introduced by McIlhiney as a quantitative method for the estimation of the purity of wood oil. If we carry the thinning still further than is recommended by McIlhiney, and use petroleum ether instead of glacial acetic acid, the addition of 0.3 per cent of iodine will give practically no additional products, but will accelerate the transformation of the oil into the insoluble elaeostearic glyceride of Fahrion.

Analytical Method No. 1.—The authors' procedure is as follows: Five grams of the oil to be examined are weighed into a small beaker, thinned with 25 cc. of petroleum ether 60 c., b. p., and the whole cooled to 0° C. After cooling, 5 cc. of ice-cold saturated solution of iodine in petroleum ether are added with stirring. Precipitation starts within a few minutes; the better the light the quicker the precipitation. After about 1 hour more petroleum ether is added and the mass stirred thoroughly. The first filtration should take place after about 3 hours, the precipitation having proceeded by that time to show a conversion of about 50 per cent of the wood oil present. Little is gained by waiting longer before filtering, as the precipitate is so heavy as to mask the further action of light upon the oil. The filtrate from the first filtration is cooled and again exposed to light. A few milligrams of iodine in solution may be added at this point if the solution has become colorless. Three precipitations with the corresponding filtrations are generally sufficient to give total yield. The solution should be kept cold at all times during precipitation, although after each filtration the extra petroleum ether may be evaporated on the steam bath if the solution be thoroughly cooled before the further addition of such and the exposure to light.

The material taken out by the third filtration is of somewhat different character from that precipitated earlier in the operation. This may indicate the presence of a third glyceride as a constituent of wood oil, and may account for the difference of opinion between Cloez,¹² who claims 75 per cent elaeomargaric acid and 25 per cent oleic acid, and Fahrion¹³ who finds 90 per cent and 10 per cent.

In Table I are compiled the data obtained by the use of this method in the examination of several Chi-

⁴Wise, *Journal of Industrial and Engineering Chemistry*, Vol. 4, p. 497 (1912).

⁵*Journal of Industrial and Engineering Chemistry*, Vol. 4, p. 496 (1912).

⁶*Chemiker Zeitung*, Vol. 31, p. 186 (1907).

⁷*Chemisches Centralblatt*, Vol. 83, p. 2154 (1912).

⁸Maquenne, *Comptes Rendus*, Vol. 135, p. 696 (1902).

⁹Andes, "Iron Corrosion and Anti-Corrosive Paints," p. 156.

¹⁰*Transactions, Chem. Soc.*, Vol. 101, p. 2082 (1912).

¹¹*Journal, Soc. Chem. Ind.*, Vol. 16, p. 195 (1897).

¹²*Proceedings, Am. Soc. Test. Mats.*, Vol. XIII, p. 946 (1913).

¹³*Boughton, Journal, Soc. Chem. Ind.*, Vol. 28, p. 719 (1909).

¹⁴*Comptes Rendus*, Vol. 81, p. 469 (1875).

¹⁵*Chemisches Centralblatt*, Vol. 83, p. 2,154 (1912).

nese wood oils and of other samples in which these oils were mixed with varying amounts of sesame and soya bean oil. The figures in the column entitled "Weight of Adulterant (calculated)" were obtained as the difference between the actual weight of the residue and the calculated weight, using 7 per cent of the weight of the wood oil in the sample as the average

TABLE I.—EXAMINATION BY PRECIPITATION OF LIGHT BREAK.

Sample No.	Weight of Sample, g.	Weight of Adulterant, g.	Kind of Adulterant.	Weight of Residue, g.	Wood Oil Precipitated (calculated), per cent.	Weight of Residue (calculated as 7 per cent), g.	Weight of Adulterant (calculated), g.	Adulterant present, per cent.	Adulterant found, per cent.
1 5.000				0.365	92.7	0.350	0.015	0.000	0.3
1 5.035				0.415	91.8	0.353	0.062	0.000	1.2
1 5.440	1.010	Sesame		1.335	94.0	0.381	0.954	15.7	14.8
1 5.160	1.000	Sesame		1.400	92.2	0.361	1.039	16.2	16.9
1 5.040	0.580	Sesame		0.920	93.3	0.353	0.567	10.3	10.1
1 5.120	0.500	Soya bean		0.815	93.8	0.358	0.457	8.9	8.2
1 5.030	1.040	Soya bean		1.400	92.8	0.352	1.048	17.2	17.3
1 5.010	1.010	Soya bean		1.330	93.6	0.357	0.973	16.8	16.1
1 4.945	1.665	Soya bean		1.920	94.8	0.346	1.574	25.2	23.8
1 6.680	0.420	Soya bean		0.940	92.2	0.468	0.472	5.9	6.6
1 5.180	0.495	Soya bean		0.825	93.6	0.363	0.462	8.7	8.1
1 5.040	0.280	Soya bean		0.650	93.1	0.353	0.297	5.3	5.6
1 6.810	1.150	Soya bean		1.470	95.3	0.477	0.993	14.5	12.5
2 5.130				0.320	93.6	0.359	-0.039	0.000	-0.6
2 5.135				0.360	93.0	0.360	0.000	0.000	0.0
3 5.135				0.300	94.1	0.360	-0.060	0.000	-1.1
3 5.600				0.360	93.6	0.392	-0.032	0.000	-0.6

NOTE.—Wood oil No. 1 was furnished by the Acme White Lead and Color Works, and is a Hankow oil of high quality. Wood oils Nos. 2 and 3 are the standard oils from the American Society for Testing Materials, and were furnished through the courtesy of Mr. H. A. Gardner and Mr. L. P. Nemzek.

weight of residue obtained from pure oil. In cases where the figures show negative, indicating an actual weight less than the calculated, the figures were inserted merely to show the extent to which the inaccuracy of the method is apparent.

The results in Table I indicate a precipitation of approximately 93 per cent of the wood oil present, when using iodine as a catalyzer. Sulphur chloride does not seem to be so efficient in its action upon the raw oils. The precipitation proceeds at a slower rate, and there seems to be a strong tendency for the material to skin over with an oxidized film during the precipitation. No quantitative results on sulphur-chloride precipitation are included in the table.

The method of estimation used in arriving at the figures given in Table I is the weighing of the final filtrate after evaporation of the petroleum ether. The amount of adulteration may be considered as the weight of the filtrate minus the amount of the residue due to the unprecipitated olein present in the wood oil. This amount of unprecipitable matter has been taken as 7 per cent of the wood oil, that amount having been shown to be an average for a number of determinations on supposedly pure wood oil.

It is possible to get an estimation of the amount of wood oil present by the direct weighing of the precipitated matter. In that case great care must be exercised to prevent oxidation of this material during drying.

The tabulated results show the possibilities of this method as a means of detecting adulteration in wood oil. It is certain that further refinement of the method is possible, which will add to its accuracy.

INSOLUBLE SOAP.

In studying the characteristics of this solid precipitated glyceride, it was noted that the potassium soap was but slightly soluble in absolute alcohol, which agrees with the findings of Normann¹⁴ and Morrell¹⁵ who worked on the material precipitated by sunlight alone. Morrell, however, also states that the soap is practically insoluble in water, which statement is not borne out by the experience of the authors.

The comparative insolubility of the potassium soap of Chinese wood oil offers possibilities of a rapid method for the detection of adulteration in wood-oil samples. The saponified product separates quite completely from absolute alcoholic potash, and may be washed free from the soap of the adulterating material. If the method be carried out at uniform temperature, preferably 0° C., and the alcohol for washing the precipitate be previously saturated with the soap, it is possible to estimate the amount of adulteration within fairly narrow limits.

Analytical Method No. 2.—A 3-g. sample of the oil to be examined is saponified with 100 c.c. of N/4 absolute alcoholic potash for ½ hour, using an air condenser of sufficient length to prevent the loss of alcohol. The saponified mixture is cooled to 0° C., held for 10 minutes at that temperature, and filtered through a Gooch crucible using a filter-paper disk instead of an asbestos pad. The precipitate, after washing thoroughly with ice-cold saturated absolute alcohol, is removed from the crucible to a cover glass, and is dried at 75 to 80° C., under vacuum, and with a stream of dry hydrogen or carbon dioxide passing through the desiccator. After cooling without removing from the desiccator, the precipitate is taken out and weighed, and the weight calculated to wood oil.

It is necessary, if the method is to be at all accurate, to use absolute alcohol both for saponification and for washing the precipitate, as the soap is appreciably soluble in the presence of even small amounts of water. This alcohol and alcoholic potash should be freely saturated with the soap before use, for although the soap is but slightly soluble in absolute alcohol, that solubility changes on standing, especially if exposed to light. It is a comparatively easy matter to keep freshly saturated solutions ready for use by making up a batch of the soap and introducing it into the stock bottles of alcohol and alcoholic potash, in quantities more than sufficient to saturate them at 0° C. When about to make a determination, the solution may be warmed until an appreciable amount of soap goes into solution,

¹⁴Chemiker Zeitung, Vol. 31, p. 188 (1907).

¹⁵Transactions, Chem. Soc., Vol. 101, p. 2,082 (1912).

after which it may be cooled to 0° C. and held for 10 minutes and filtered. This fresh filtrate is ready for use, and the fact that the procedure followed will be duplicated on the saponified sample helps to insure the accuracy of the determination.

During the washing of the precipitate the whole must be kept cold, for the solubility of the material in alcohol is greatly increased by a rise in temperature. This is accomplished by filtering through a Gooch crucible surrounded by cracked ice. The authors have found the apparatus shown in Fig. 1 to be quite satisfactory.

The precipitate is susceptible to oxidation and must be kept away from air during drying. Also, the fact that high temperature will char the soap limits the drying temperature to about 80° C. The precipitate

ing the results for this table it was decided to accept the weight of the dried insoluble soap as representative of the weight of wood oil present in the sample, since the error of this assumption was considered to be within the limits of error of the method.

Although neither of the above methods has proved entirely satisfactory as a method for the estimation of wood oil in rosin varnishes, the efforts made to apply

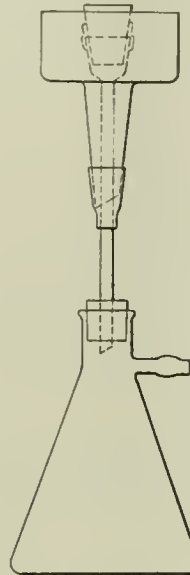


Fig. 1.

them to that end have resulted in some interesting data regarding the conditions existing in this type of varnish.

An examination of the separated constituents of a Chinese-wood-oil rosin varnish seems to show that the polymerization of wood oil in the presence of rosin is practically as complete as in the oil, subject to the same heat treatment in the absence of rosin. The fatty acid in each case shows a molecular weight double that of the fatty acid of raw wood oil. The difference in characteristics between these two polymerized products has not as yet been satisfactorily accounted for.

A comparison of the molecular weights of the fatty acids from raw wood oil and the light breaks seems to show that this light break is an isomer rather than a polymer, and that there is practically no difference between the light break formed slowly by sunlight alone and that catalyzed by iodine.

TABLE II.—EXAMINATION BY PRECIPITATION OF INSOLUBLE POTASSIUM SOAP.

Sample No.	Weight of Sample, g.	Weight of Adulterant, g.	Kind of Adulterant.	Weight of Soap, g.	Weight of Wood Oil (calculated), g.	Wood Oil Recovered, per cent.	Weight of Adulterant Found, g.	Adulterant Found, per cent.	Adulterant Present, per cent.
1	3.301			3.334	3.334	101.0	-0.033	-1.0	
1	2.814	0.304	Linseed	2.807	2.807	99.8	0.311	9.9	9.8
1	3.012	0.180	Linseed	3.021	3.021	100.3	0.171	5.5	5.6
1	2.516	0.506	Linseed	2.508	2.508	99.8	0.514	17.0	16.7
1	3.138			3.170	3.170	101.0	-0.032	-1.0	
1	2.859	0.959	Soya bean	2.874	2.874	100.6	0.944	24.7	23.8
1	2.642	0.881	Soya bean	2.645	2.645	100.1	0.878	24.9	25.0
1	3.013			3.006	3.006	99.8	0.007	0.2	
1	3.006	0.167	Soya bean	2.982	2.982	99.2	0.191	6.0	5.3
1	2.051	1.302	Soya bean	2.020	2.020	98.1	1.333	39.8	38.9
1	2.461	0.125	Linseed	2.536	2.536	103.0	0.075	2.9	4.8
1	2.791	0.607	Linseed	2.883	2.883	103.3	0.515	15.2	17.9
1	2.742	0.380	Linseed	2.761	2.761	100.7	0.361	11.5	12.2
1	2.742	0.183	Linseed	2.741	2.741	100.0	0.184	6.3	6.3
1	2.528			2.501	2.501	98.9	0.027	1.1	
1	2.524			2.550	2.550	101.0	-0.026	-1.0	
1	2.521			2.510	2.510	99.5	0.011	0.5	
1	2.510			2.514	2.514	100.2	-0.004	-0.2	
1	2.321	0.707	Linseed	2.367	2.367	102.0	0.661	21.8	22.4
1	2.428	0.738	Linseed	2.508	2.508	103.3	0.658	20.8	23.3
1	3.019			3.019	3.019	100.0			
1	3.039	0.409	Mixed	3.025	3.025	99.5	0.423	12.3	11.9
1	3.199	1.049	Mixed	3.201	3.201	100.3	1.038	24.5	24.7
2	3.252			3.224	3.224	99.1	0.028	0.9	
3	3.471			3.544	3.544	102.1	-0.073	-2.1	
4	3.156			3.014	3.014	95.5	0.142	4.5	
4	3.190			3.092	3.092	96.9	0.098	3.1	

NOTE.—Wood oil No. 1 was furnished by the Acme White Lead and Color Works, and is a Hankow oil of high quality. Wood oils Nos. 2 and 3 are the standard oils from the American Society for Testing Materials, and were furnished through the courtesy of Mr. H. A. Gardner and Mr. L. P. Nemzek. Wood oil No. 4 was furnished by Mr. L. P. Nemzek, representing the Educational Bureau of the Paint Manufacturers' Association. This oil is from American-grown nuts.

may be dried in a desiccator connected by a long rubber tubing to a source of hydrogen or carbon dioxide, and to a vacuum pump. After introducing the precipitate to be dried, the desiccator may be placed in a low-temperature steam drying oven for 3 hours.

The results obtained by the use of the insoluble-soap method and the data from which these results were computed, are compiled in Table II. In calculat-

An oil refiner in Rosario, Argentine, has been carrying out a series of experiments for the manufacture of oil from the seed of the grape. The result so far has been satisfactory, and an oil in excellent condition for the manufacture of soap has been obtained. At the request of the Mendoza Government this gentleman has now gone to that Province to carry out further experiments. If the result proves satisfactory the new invention will be of considerable importance to the wine industry, as hitherto the seeds have been treated as waste.

BOOK REVIEWS.

Fixation of Atmospheric Nitrogen. By Joseph Knox, B. Sc. Published by the D. Van Nostrand Co., New York. Price, 75 cts.

This book is one of a series of chemical monographs now being published by the Van Nostrand Co. This book covers a field which is of particular interest at the present time as there have been many advances recently made in the fixation of atmospheric nitrogen. This monograph reviews all of the processes which are of any commercial importance giving them under three headings:

1. Fixation of Atmospheric Nitrogen as Nitric and Nitrous Acids or their Salts.
2. Synthesis of Ammonia and Ammonia compounds from Atmospheric Nitrogen.
3. Conversion of Atmospheric Nitrogen into compounds which readily yield Ammonia.

The monograph also contains a bibliography covering five pages which cites authorities used in the preparation of this work.

Organometallic Compounds of Zinc and Magnesium. By Henry Wren, M. A., B. Sc., Ph. D. Published by the D. Van Nostrand Co., New York. Price, 75 cts.

This is the first in the series of chemical monographs brought out by the D. Van Nostrand Co. and covers the organometallic compounds of Zinc and Magnesium. The methods of preparing these compounds are cited, together with the properties of the compounds. The monograph cites in each instance, the investigators by whom the compounds have been prepared, and in the accompanying bibliography is mentioned the original source in which the article by the experimenter appears.

Water, Its Purification and Use in the Industries. By William Wallace Christie. Published by the D. Van Nostrand Co., New York. Price, \$2.00.

This publication gives, primarily from the engineer's standpoint, the purification of water for industrial purposes. It describes the various systems employed for water softening, and also some of the methods employed in the clarification and sterilization of water for drinking purposes. The book is particularly good in its illustration, and in its descriptions of the apparatus employed in water treatment. From a chemical standpoint, it, however, leaves considerable to be desired in its comments on various reactions which may be employed for the purposes enumerated and in comments on the re-agents which may be employed. The book is particularly commended to the chemist who desires to increase his knowledge of the mechanical appliances used in water treatment.

Modern Research in Organic Chemistry. By F. G. Pope, B. Sc. Published by the D. Van Nostrand Co., New York. Price, \$2.25.

The author has grouped the compounds described in nine different chapters with headings as follows:

- I. The Polymethylenes.
- II. The Terpenes and Camphors.
- III. The Uric Acid or Purine Group.
- IV. The Alkaloids.
- V. The Relation between the Color and Constitution of Chemical Compounds.
- VI. Salt Formation, Pseudo-Acids and Bases.
- VII. The Pyrones.
- VIII. Ketens, Ozonides, Triphenylmethyl.
- IX. The Grignard Reaction.

The book is commended to the student of organic chemistry as one in which most of the methods employed in the preparation of the compounds enumerated are given, and for the completeness with which the various reactions of these compounds are given. Particularly interesting is the discussion of the development of the formulas and chemical constitution of the various organic bodies enumerated.

Manual of Cement Testing. By William Allen Richards, B. Sc. and, Henry Briggs North, B. Sc. Published by the D. Van Nostrand Co., New York. Price, \$1.50.

The object of the authors of this book as cited in their preface, is to assist in bringing about a uniformity in the testing of cement. The first chapter classifies the cements, describes very briefly their manufacture and composition. Following this, come chapters on sampling, determinations of fineness, specific gravity, and other physical tests which are applied to cement. Part Two gives the method of cement analysis as endorsed and published by the Committee of the American Society of Civil Engineers. The book is of value in that it gathers together under one cover methods of testing which have heretofore only been available in various publications of the American Society of Civil Engineers, The Society for Testing Materials, the Association of the American Portland Cement Manufacturers, etc.

Chemistry of the Rubber Industry. By Harold E. Potts, M. Sc. Published by D. Van Nostrand Co., New York. Price, \$2.00.

This book is one of a series of volumes issued by the D. Van Nostrand Company under the general title "Outlines of Industrial Chemistry." The series is edited by Guy D. Bengoff, M. A., M. Sc. The general object of this series is to bridge over the information supplied in our books in chemistry and supplemented by a description of the processes in which the chemical theories are applied.

This particular volume on the chemistry of the rubber industry begins with a chapter on Colloidal Chemistry as a knowledge of this subject is deemed of particular importance in the study of the behavior of rubber solutions. Various steps in the preparation of rubber from the raw state to the various products in which it is placed on the market, is then given. A very

complete discussion is given of the bases of the chemistry of the various processes employed, and in each instance where more than one theory has been advanced, a clear statement of each theory is given so that the reader will be able to form his own judgment as to which is the most probable.

Methods of analysis as applied to raw rubber and also as applied to manufactured rubber are given. The feature to be commended in the description of these methods of analysis is the discussion of the faults inherent on certain methods of analysis and comments on how errors arising from them may best be avoided.

Solvents, Oils, Gums, Waxes and Allied Substances. By Frederick S. Hyde, Ph. B. Published by the D. Van Nostrand Co., New York. Price, \$2.00.

The author states that these notes are for the use of factory chemists and others who may desire a short reference book on commercial organic products and only those methods and tests which seemed reliable in the mind of the author have been selected. The subjects covered are various solvents used for the gums and resins, terpene bodies, true gums, carbohydrates, albuminoids and proteids, and all fats and waxes.

The Chemistry of the Oil Industries. By J. E. Southcombe, M. Sc. Published by the D. Van Nostrand Co., New York. Price, \$3.00.

The author of this book has attempted to condense into 200 pages a large portion of the material which is given in Lewkovitsch's two volumes on Oils, Fats and Waxes, and has included in addition, a chapter on the mineral oils. He has, however, omitted a description of the mineral and vegetable oils as given by Lewkovitsch.

The book is very well prepared and very well written and gives briefly, as well as clearly, the chemistry of the various oils under discussion. A description of the methods of preparing various oils is given together with the analytical tests which are commonly applied to them.

Laboratory Manual of Glass Blowing. By Frances C. Frary, Ph. B. Published by the McGraw-Hill Book Company, New York. Price, 75 cts.

This book should be in the hands of every laboratory worker as it provides a clear and detailed discussion of the elements of glass blowing and it will enable any worker, after a short practice, to make the necessary repairs in class apparatus which must be used in his laboratory. No attempt is made to describe the more complicated work of glass blowing but very clear and concise directions are given for the handling of the ordinary operations of glass blowing. This little book is commended to all laboratory workers.

Principles of Quantitative Analysis—An Introductory Course. By Walter C. Blasdale, Ph. D.

Published by D. Van Nostrand Co., New York. Price, \$2.50.

There are so many text books on quantitative analysis appearing at this time that a new book on this subject must show some decidedly new features in order to receive consideration from the instructor in chemical analysis and from the chemical practitioner.

The text of Dr. Blasdale should, on this account, receive consideration. It contains the ordinary quantitative determinations which are included in the common text books on this subject, and in addition to these contains such work as an analysis of brass, of black powder, the determination of caffeine in tea, the determination of potassium bitartrate in argol, and the determination of boric-anhydride in the natural borate.

The introduction to each chapter is also commended as in this introduction is included the chemical theories of analytical portions which are to follow. Chapters are also introduced on the preparation of substances for analysis, the properties of solutions, factors which determine chemical equilibrium, the chemical activity of electrolytes, methods of producing and applying heat, the removal of undesirable constituents by evaporation, and on the calculation of results.

Qualitative Chemical Analysis. By Wilfred Wel-day Scott, A. M. Second Edition. Published by D. Van Nostrand Co., New York. Price, \$1.50.

The author, so far as the reviewer can determine, has presented no new ideas on the subject of qualitative analysis, and the book must therefore be classed with the large number of similar books on the same subject which present qualitative analysis in the same way. It appears to be no better nor any worse than the customary text book on this subject.

Electrical Conductivity and Ionization Constants or Organic Compounds. By Hayward Scudder, B. A., B. S., M. D. Published by D. Van Nostrand Company, New York. Price, \$3.00.

This book gives numerical data for the ionization constants at all temperatures at which they have been measured, and includes some numerical data of electrical conductivity. Also contains a bibliography of the periodical literature from 1889 to 1910 inclusive. This book undoubtedly represents a large amount of labor on the part of the author in collecting this data from various sources. It is a book which will be invaluable to the laborer in the field of organic chemistry.

Detailed Report on Preston County. Issued by the West Virginia Geological Survey.

This report was issued under date of Sept. 1, 1914. It contains 566 pages +XIX of introductory matter, and is illustrated with 49 halftone plates and 10 figures in the text; also a case of 3 maps covering the soils,

topography and geology of the county separately. In addition to the detailed description of all the geologic formations exposed in Preston County, the geologic map gives the structural contours and outcrop of the Upper Freeport coal, the most important mineral horizon of the area in question. The soil and topographic maps will also prove of great value to every interest including agriculture, road improvement, water resources, etc. Price, with case of maps, delivery charges paid by the Survey, \$2.00, but for combination price with other publications, write to the W. Va. Geological Survey, P. O. Box 448, Morgantown, W. Va. Extra copies of the Topographic map, 50 cts. each; and of the Geologic map, \$1.00 each.

Quantitative Chemical Analysis. Introductory Notes.—By Chas. Wm. Foulk. Third edition. Published by McGraw-Hill Book Co., New York. Price \$2.00.

The author states in his preface that he "aims to present the beginning work in quantitative analysis in such a way that the student will be lead to think more of the general aspects of the subject than learning merely to carry out his section of methods." If the author has been able to accomplish this in his text book, he is to be highly commended. Considerable discussion is given the theory involved in the operations which are conducted. Some points not commonly taken up in the textbooks on quantitative analysis are given attention. The author has utilized the first 130 pages, which is more than half the book, in a general discussion of the laboratory operations involved in quantitative analysis. Much of this discussion seems to the reviewer to be of doubtful value. It is a common experience of instructors in quantitative analysis that students must learn the manipulations by practice and by instructions given at the time laboratory operations are being carried out, and that any lengthy discussion of laboratory technique in advance of its actual performance is undesirable.

Laboratory Experiments in General Chemistry.—By H. B. North, Ph. B., B. Sc. Published by the D. Van Nostrand Co., New York. Price \$1.00.

It is the reviewer's opinion that this book is another of the many laboratory manuals in General Chemistry appearing on the market, the only excuse for the publication of which is the desire of some instructor to present his particular method of giving instruction to his students before the public. There is no new material presented in the text, nor is the old material presented from any new viewpoint.

It is stated that the production of the gold mines of India during the first six months of 1914 amounted to 293,577 ounces, as compared with 289,991 ounces during the corresponding period of 1913.

CIVIL SERVICE EXAMINATIONS.

FOOD CHEMIST.

The Illinois Civil Service Commission will hold an examination for Food Chemist Nov. 7, 1914, at 15 points in Illinois. This examination is open to residents of the state from 21 to 50 years of age. The starting salary is \$100 a month, and there is possibility of increase to \$150 a month. Several vacancies now existing will be filled from the eligible list resulting from this examination. Food chemists are employed in the work of the State Food Commission. Under the direction of the State Analyst they analyze food stuffs to determine whether constituents prohibited by law are present; they also act as witnesses in prosecutions. Education equivalent to graduation from a chemistry course in a college of recognized standing is necessary. Applications must be on file at the office of the Commission in Springfield not later than 5 p. m., October 28. The proper forms may be secured by addressing the State Civil Service Commission, Springfield, Ill.

ASSISTANT IN NUTRITION AND HYGIENE.

The U. S. Civil Service Commission will hold an open competitive examination for assistant in nutrition and hygiene, for men only, on Nov. 18. From the register of eligibles resulting from this examination certification will be made to fill a vacancy in the position of assistant in nutrition investigations in the Office of Experiment Stations, Department of Agriculture, Washington, D. C., at a salary of \$1,440 a year, and vacancies as they may occur in positions requiring similar qualifications, unless it is found to be in the interest of the service to fill any vacancy by reinstatement, transfer, or promotion. The duties of this position will be laboratory work by physical, microscopical, and other methods on questions of food, clothing, and household equipment, particularly in their relation to the improvement of home conditions. The appointee will also be expected to help in preparing material for publication. Persons who desire this examination should at once apply for application Form 1312, stating the title of the examination for which the form is desired, to the U. S. Civil Service Commission, Washington, D. C.

JUNIOR CHEMIST IN RADIOACTIVITY.

The U. S. Civil Service Commission will hold an open competitive examination for junior chemist in radioactivity, for men only, on Nov. 4. From the register of eligibles resulting from this examination certification will be made to fill vacancies in this position in the Bureau of Mines, at Denver, Colo., at salaries ranging from \$1,200 to \$1,500 per annum, and vacancies as they may occur in positions requiring similar qualifications, unless it is found to be in the interest of the service to fill any vacancy by reinstatement, transfer, or promotion.

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NOTES AND COMMENTS.

Chances for Increasing American Manufacture of Chemicals.

There was a conference called recently in Washington, presided over by Secretary Lane of the Interior Department, and attended by representatives of finishers of cotton fabrics, manufacturers of coal tar products, manufacturers of aniline dyes, wholesale drug houses, the largest American chemical companies, the Standard Oil Company, and the Smet-Solvay Company. The object of the conference was to ascertain whether it would be best for the government of the United States to give any aid in bringing about the production in this country of some, at least, of the coal tar products and other chemical products that have been imported in times preceding the European war. A wide field was covered in the discussion and suggestions as to what might be done, including also some reference to legislation now pending in Congress in regard to the utilization of foreign patents not now being operated in this country. The conclusions and suggestions adopted by this conference of representative interests are as follows: First—That there should be a system instituted in this country similar to the one in England whereby if a foreign

patent is not used and manufactured within a reasonable time, it will be open to use by American manufacturers. Second—A law should be passed whereby unfair competition will be cut off. This relates to the practice known as "dumping." This would preclude the practice, which it is alleged is now followed by manufacturers, of selling foreign products in this country below the cost of manufacture. It was thought by all representatives of the manufacturers present that it was not profitable to go into the manufacture of aniline dyes at the present time, for the reason that a demand could not be secured for a sufficient amount of American dye-stuffs. The conference adjourned without being able to make any specific recommendations as to how present conditions might be bettered, the general opinion being that nothing could be done to better the present situation.

Uranium-Bearing Minerals in India.

Little is known and little published with regard to the existence of pitchblende and uranium ore in India, though at Singar, in the Gaya district, a Calcutta firm, Messrs. Moll Schutte & Co., has mine holdings from which some quantity of pitchblende has been obtained. According to Vice Consul General John Stuart Hunt, Calcutta, the locality was inspected a few months ago by a member of the Geological Survey of India, and he reports most favorably on the ores and uranium-bearing substances found. It has been a matter of interest to watch developments in the prospecting for this very important and valuable mineral, for the fact that the world's supply of radium is limited is well known. It is also known how keen is the search for this precious substance and how high the value placed upon it by scientists and doctors.

The investigations conducted by Messrs. Moll Schutte & Co. have been so successful that it has been decided to form a "radium syndicate" to acquire from that firm, as representing the holders of two mining leases, the option of taking up the mining rights over an area of 5 square miles, representing a portion of the area comprised under these two leases, which have been granted by the Rajah of Singar for the prospecting and working of pitchblende and other valuable minerals which are known to occur in the area. The option to be acquired by the syndicate will be for a period of one year from July 1, 1914. The syndicate, the capital of which will be \$16,222, will prospect and develop the property in question with a view, during the period of the option, of floating a company on such terms as may hereafter be arranged. The raising of the money required by the syndicate is assured. European scientists are showing a keen interest in the samples of pitchblende obtained, and the analysis reports show a very high percentage of radioactive constituents. If the expectations of the syndicate are realized, and there is every reason to believe they will be, India will become the home of an industry of first im-

portance to the scientific and medical world. A Calcutta publication says:

There is probably no other substance of scientific interest and practical value which is at the same time so valuable and so scarce. One eminent professor of European reputation reports that he is looking for uranium mineral with rather special composition to try to test a certain point of scientific interest and thinks there is a fair chance that the Indian mineral will meet this requirement.

A point of great interest in India is the possibility of using locally obtained radioactive earth for medical purposes at home, as at present supplies for this purpose are obtained abroad. This radioactive earth is not an expensive substance and is reported to have been very effective in cases in which it has been employed by some of the local doctors. A considerable quantity of this earth has been obtained from the area to fall under the control of the "radium syndicate," and experiments are now in progress with a view to determining whether the local product might not prove an effective substitute for the imported article.

Potash Shipments from Belgium.

The State Department at Washington is in receipt of a note from the American Legation in Belgium, in which it is stated that the shipment of potash (Ger-

impression that certain European waters have medicinal properties not possessed by any American waters, and many persons addicted to the Apollinaris, Clysmic, or Celestine-Vichy habit might be equally satisfied by waters from American springs in bottles of American glass, bearing labels printed in the United States.

Tungsten Mines in Chosen.

Vice Consul General Raymond S. Curtice, Seoul, reports that during the last calendar year operations were commenced in the tungsten mines discovered in the eastern part of Chosen. An average of 5 tons per month, it is reported, was shipped to Yokohama, the estimated value being \$400 per ton. Numerous applications are being received for permission to work similar mines in the same section of the country. However, owing to the general scarcity of tungsten and to the probable need of such supplies as exist for the development of the iron industry in Chosen, it is reported that the authorities are at present not granting permits for such mines.

American Purchases of Artificial Dyestuffs.

The imports of artificial dyestuffs into the United

TABLE I.

	1912.		1913.		1914.	
	Pounds.	Value.	Pounds.	Value.	Pounds.	Value.
Alizarin and alizarin colors:						
From Germany	5,373,087	\$1,359,560	7,976,457	\$1,797,086	2,593,758	\$833,705
From all other countries.....	75,662	22,376	60,135	20,184	39,656	11,754
Aniline salts:						
From Germany	4,252,143	337,005	4,545,798	337,832	2,768,191	202,722
From all other countries.....	548,276	45,671	418,569	32,461	316,276	20,006
Indigo:						
From Germany	7,032,023	965,047	7,212,451	974,502	7,448,412	938,097
From all other countries.....	626,044	188,095	500,057	128,395	676,799	155,129
Coal-tar colors, all other:						
From Germany		5,757,052		5,766,600		5,965,537
From all other countries.....		1,208,069		1,338,684		1,275,869
Total values:						
From Germany		\$8,418,664		\$8,876,020		\$7,940,061
From all other countries.....		\$1,464,211		\$1,519,724		\$1,462,758

NOTE.—The statistics for indigo include imports of natural indigo from India, which average less than \$100,000 worth annually.

man) from the port of Antwerp is now allowed; that no prohibition is placed on vessels clearing from Belgium.

American Mineral Waters.

Annual imports of mineral waters into the United States are over 3,000,000 gallons, having a value of nearly a million dollars. Two-thirds of these imports come from Germany, France, and Austria-Hungary, and as soon as the stocks on hand are consumed domestic waters should take the place of those derived from foreign springs. In this connection it is interesting to note that last year the reported sales from 838 commercial springs in the United States were more than 57,000,000 gallons, having a total value of \$5,500,000. The United States Geological Survey suggests that there is a somewhat popular but fallacious

States, according to the Daily Consular and Trade Reports, have been stationary for over five years, with a slight decline during the fiscal year ended June 30, 1914. The total average purchases from abroad of alizarin and coal-tar colors have been about \$10,000,000 annually, but there was a drop in the year just closed to \$9,500,000. The imports during the past three fiscal years ended June 30, with the share furnished by Germany, are shown in Table I.

The textile and other industries in the United States have been steadily increasing their consumption of synthetic dyestuffs, but the large increase has been supplied from the new and enlarged chemical works in the United States, the value of whose output was \$7,350,748 in 1899, \$10,912,224 in 1904, and \$16,428,676 in 1909.

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THE COAL AND CLAY RESOURCES OF NORTH DAKOTA.*

By EARLE J. BARCOCK,†

Although North Dakota is not a metal producing state and may never become a *great* mining state, it certainly possesses some mineral resources, especially its great coal and clay deposits, which are sure to become more extensively used and to prove of great economic value. The research, discovery, and development of the best methods for the utilization of these resources require time, patience, hard work, and technical skill. But these efforts are gradually leading to not only a more economical and wider use of these resources but also to the establishing of associated industries.

COAL.

Something is known of the vast deposits of lignite coal which are found within the state of North Dakota, but it is surprising how little the immense value of these deposits is appreciated. There is a very large area in the western part of this state which is underlaid with quite thick deposits of lignite coal. Whether the outcrops which have been discovered are fragments of one immense coal basin which has been broken up by water action and covered by newer formations, or whether they are deposits of numerous woody swamps of the same geological period, we may not at present determine with certainty, but we may be sure that North Dakota has enough coal, if properly used, to supply her fuel needs for generations.

North Dakota has one of the largest coal areas of the states of the Union, estimated at 32,000 square miles and capable of producing probably 500 billion tons. While many mines have been opened in different localities, the deposits are for the most part undeveloped. Although these deposits are in a general way similar, still they vary somewhat in both physical and chemical properties in different localities. Usually the coal is of a brownish, black color, seldom having much lustre. Occasionally, however, seams are encountered which are more compact and have a darker color and brighter lustre. The seams most commonly worked

usually appear at from 50 to 200 ft. below the surface and vary in thickness, being from 7 to 20 ft.

From many hundreds of analyses of lignite coal made in the laboratories of the School of Mines at the University of North Dakota, the average composition of the dried coal would seem to be about as follows:

Dried Coal.	Approximate average.
Fixed carbon	47 per cent
Volatile matter	44 per cent
Ash	9 per cent

Moisture in coal fresh from the mine runs from 25 to 35 per cent.

It is evident from the investigations which have been carried on at the School of Mines that the heat value or calorific power of the average lignite of North Dakota, when entirely dry, is about 65 per cent of that of the Hocking Valley coal, and about 60 per cent of that of the Pocahontas coal. The analyses which have been made show that the fixed carbon in the samples of North Dakota coal (dried) usually runs from 48 to 52 per cent; that of West Virginia bituminous coals about 67 per cent; that of the better grades of semi-bituminous dry coals of Maryland 75 per cent; and that of the fine, dry, close burning bituminous coals of Pennsylvania 70 per cent. In a general way it may be said that the heating power of one ton of North Dakota coal will equal about 65 per cent of a ton (1,300 lbs.) of bituminous coal.

The purity of a fuel is a very important element in determining its value. A difference of 2 or 3 per cent in the earthy matter of two coals may be the source of a very serious difference in their final value. North Dakota coals are almost always very free from earthy matter as seen from the amount and character of their ash.

By these comparisons it will be seen that North Dakota lignite ranks, so far as its heat producing power is concerned, between the lower grades of lignite and a bituminous coal, and that it is far superior to the lignite mined in some countries.

It is largely due to a lack of familiarity with the character of lignite coal and to a lack of knowledge of the best methods of burning it, that this coal is not being more generally used. However, the use is gradually being extended as from time to time more perfect methods of burning appear.

At the present time lignite coal is chiefly used in

*From The Quarterly Journal of the University of North Dakota.
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lumps in heating and cooking stoves and in engines for power. It is generally used in the most simple manner and very few special methods have been adopted for burning or utilizing this coal or for preparing it for the market. But there can be little doubt that for general stove and furnace use briquetted lignite would prove a most economic and profitable fuel.

A successful and sufficiently inexpensive method for commercial briquetting of lignite is now being developed at the School of Mines. The process is made commercially possible and profitable by operating the briquetting in conjunction with a gas producing plant in which a variety of by-products are saved and utilized and by which process the residue after the gas has been driven off can be successfully briquetted into a concentrated and valuable fuel.

One ton of the dry lignite will produce about two-thirds of a ton of briquets, in addition to about 8,000 to 10,000 cubic feet of gas and other valuable by-products such as tars, ammonium sulphate, etc. Considering the ease with which the gas is produced, the low cost of the original lignite, and the value of the residue, this gas should have a large commercial value for heating and power purposes because of the low price for which it could be obtained if manufactured in a plant used also to produce briquets from the residue.

The briquets present many advantages over the original lignite or even over other varieties of coal. They have nearly double the heating value of the original lignite, they do not disintegrate on standing or burning, can be stored without being affected by atmospheric conditions, and are uniform in size and convenient to handle.

There seems little doubt but that the briquetting and the production of gas from lignite will in the near future be put on a commercially satisfactory basis in this state. While this will prove of great value to all parts of our state, it will be especially important to those communities nearest the great lignite deposits in the western portion of the state, for in some of these the wastes can be converted into electricity which in turn can be sent to surrounding towns and villages, thus distributing power and light from numerous central power plants. Such an arrangement will not only be a great saving of our fuel resources but will also result in establishing many industries which can be developed by abundant and cheap electric power.

CLAY.

Among the mineral resources of the state, the clays are second only in extent and economic value to our coal deposits. North Dakota is remarkably well supplied with a variety of valuable clays suited to the manufacture of many important products. These deposits are quite extensive, especially in the western portion of the state, and many of them are found not far from the lignite coal beds, a fact which will greatly enhance the value of both deposits.

There is an unusually large number of varieties of clays found in this state ranging from common brick clay to deposits suited to the production of a very high grade art pottery. A great deal of work has been done at the School of Mines in the testing of these clays and in making them into a variety of products for which they are found adapted, such as brick, terra cotta, paving brick, fire brick, and other refractory materials, drain tile, stoneware, sewer pipe, earthenware, and the higher grades of art pottery. Clays are found well suited to the manufacture of all of these products and many of them are of exceptionally high grade. As an illustration I give the following analysis of white earthenware clay from North Dakota:

	Per Cent.
Silica	70.27
Alumina	20.81
Iron oxide	0.33
Calcium oxide	0.23
Magnesium oxide	0.26
Loss on ignition	6.38

As will be seen by referring to the above analysis, some of the clays of North Dakota are of unusual purity and also are remarkable in having a composition, in their natural state, very similar to many of the artificially prepared clay bodies, used in potteries, which have been built up to their proper composition, often by the use of several mixtures. For example the following analysis is of a sample of the artificially prepared mixture just ready to go to the molds in one of the large eastern factories:

	Per Cent.
Silica	69.03
Alumina	23.89
Iron oxide	0.45
Calcium oxide	0.29
Magnesia	0.05
Loss on ignition	7.46

By comparing this analysis with that of the North Dakota white earthenware clay it will be seen that the sample of North Dakota clay as dug, is very pure and that there is a striking similarity in composition to that of the artificially prepared pottery mixture referred to. And as might be expected, many of the high grade clays of this character from the state are capable of producing pottery and other clay products of exceptionally high quality. Few people appreciate the remarkable character of many of the clays of western North Dakota and the important part they are to play in the future development of the state.

The proper development and utilization of the great coal and clay deposits of North Dakota and the use of lignite for the production of cheap power and electricity by the introduction of by-product gas and briquetting plants, and by other means of utilizing these resources, will result in saving large sums of money for the people of this state and in the introduction of a variety of manufacturing industries, a condition which will add greatly to the stability and prosperity of a region already well known for its agricultural resources and possibilities.

THE ORIGIN, MINING AND PREPARATION OF PHOSPHATE ROCK.*

By E. H. SELLARDS.†

Phosphate rock like most other mineral substances is found in nature in varying degrees of purity. Of the impurities that are present some are constituents of the rock itself; others are inclusions of a foreign substance within the rock; while still others represent merely associated materials or minerals, either clinging to the rock or found in cavities and natural depressions, and hence largely removed in mining. Some of these impurities are distinctly deleterious to the processes of manufacture for which the phosphate is mined, while others, although neutral in action or nearly so, yet by their presence reduce the average grade of the rock and thus add useless bulk to the shipment.

It is the object of refined processes of mining to bring the product, as delivered from the mine, to the highest possible grade consistent with the market requirements and demands. This, however, is not accomplished without actual loss in the form of discarded phosphate. It is evident, therefore, that the devising of methods for reducing this loss in mining, and yet maintaining the grade of the rock which the market requires, is one of the serious problems that the producers have to face.

MINERALS OF PHOSPHATE ROCK.

The minerals included under the term "phosphate rock" are the calcium phosphates. Of these, apatite is perhaps the most definite and constant in composition, although of this mineral two varieties are recognized, namely, fluorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$, and chlorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$. Moreover, the calcium of this mineral may be partly replaced by manganese, forming yet another mineral, manganapatite; or the mineral may become hydrated forming hydroapatite, which is found as mammillary deposits often not unlike chalcedony in appearance. The term "phosphorite" has been applied to the massive amorphous deposits of phosphate, which may be compact, earthy or concretionary.¹ Among other varieties of apatite may be mentioned staffelite, which contains a small percentage of both iron and aluminum. It is of interest to note also that this variety is believed to result from the action of carbonated waters on phosphorite, and hence is likely to occur incrusting ordinary phosphate rock acted upon by carbonated waters. Another variety, pseudoapatite, contains both sulphur and carbon dioxide. Of the many other calcium phosphate minerals

some closely approximate apatite while others grade into compounds so variable and indefinite in composition as scarcely to be classed as minerals. The deposits of phosphate found in nature evidently contain a number of calcium phosphate minerals, the constituent impurities of which affect the market value of the rock. The aluminum phosphate, wavellite, should also be mentioned since it is mined to some extent as a source of phosphorous.

ASSOCIATED MINERALS.

Various other minerals in nature are found associated with the calcium phosphates. This association is sometimes due to actual relationship between the minerals. On the other hand, the association of minerals may be purely accidental, or incidental to the manner of formation of the deposits. With regard to the related minerals, it is apparent that where the calcium phosphates are abundant, other phosphates are likely also to occur. In fact it is scarcely to be expected that extensive calcium phosphate deposits will be found without the presence of at least a limited amount of other phosphate minerals. This is particularly true of iron and aluminum phosphates. These two bases are widely disseminated in nature, and moreover they combine readily with phosphoric acid to form phosphates. Of the iron phosphates, the mineral vivianite, although occurring in relatively small quantities, is widely distributed in nature, and may occur in limited quantities in phosphate deposits, usually as an incrustation, or as an alteration product of other minerals. The iron minerals frequently form in bogs, and it is an observed fact that the phosphate deposits in such localities not infrequently contain more iron than do the same deposits when found on the uplands. In such cases the iron is doubtless a comparatively recent infiltration, and may include phosphates of iron as well as oxides and other iron minerals. Of the aluminum phosphates a large number are known, one of which, wavellite, as already stated, is mined as a source of phosphorus. This mineral and others of the aluminum phosphates are likely to occur in association with calcium phosphate.

Some of the large phosphate deposits have been formed by the replacement of an original rock by calcium phosphate. In this process parts of the original rock not infrequently remain unchanged or incompletely phosphatized. Since the phosphatizing processes proceed from the surface, the imperfectly phosphatized remnant is likely to lie within the rock, thus giving rise to included impurities that are difficult to eliminate. Moreover small amounts of clay and silica are usually found in the limestone, and as these substances do not readily phosphatize, if not leached out, they remain as impurities in the rock.

Aside from these related minerals, the materials associated with the phosphate rock are varied in character. They include clay, fragments of limestone, flints, gravel, silica in the form of sand, and other re-

*From Transactions American Institute of Mining Engineers.
†Tallahassee, Fla.

¹Dr. Austin F. Rogers, who is investigating phosphate minerals, states that phosphorite or phosphate rock seems to be a mixture of two minerals, amorphous collophanite, largely a solid solution of calcium carbonate in calcium phosphate, and crystalline dahllite, a calcium carbonophosphate with the formula $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaCO}_3$, analogous to fluorapatite. The amorphous collophanite gradually changes to the crystalline dahllite. (Personal letter of May 23, 1914.)

sistant materials, the character of which is determined by the manner of formation of the deposits. The associated materials of this nature make up the matrix in which the phosphate rock is imbedded. It is scarcely possible in mining to remove entirely all associated minerals, and the purity of the rock as delivered to the market is affected, without doubt, by the presence of more or less of these minerals, as well as by the constituent impurities of the rock.

OBJECTIONABLE IMPURITIES.

Of the impurities contained in or associated with phosphate rock, the most objectionable in the processes of manufacture of acid phosphate for fertilizers, for which purpose the phosphate rock is almost wholly used, are iron and aluminum. For this reason practically all phosphate mined is sold under a guarantee that the combined iron and aluminum expressed as oxides, do not exceed a given small percentage of the whole, from 2 to 4 per cent being allowable. Iron when present in excess of about 2 per cent brings about reactions which result in the formation of a gelatinous substance injurious to the mechanical condition of the mixture, occasioning also a loss of soluble phosphoric acid. A first step in the reaction with the iron is probably as follows: $2\text{FePO}_4 + 3\text{H}_2\text{SO}_4 = 2\text{H}_3\text{-PO}_4 + \text{Fe}(\text{SO}_4)_3$. Of the sulphate of iron thus formed, a part, according to Fritsch,² reacts on acid phosphate of lime thus forming the objectionable gelatinous precipitate. Owing to the demand of calcium sulphate for water, hydrated iron phosphate, which is a product of these reactions, may subsequently become dehydrated and insoluble, thus causing the loss of available phosphoric acid.

Aluminum existing as a silicate in phosphate rock is likely to be injurious, since according to Fritsch, if not decomposed by the acid, it may cause a part of the phosphoric acid to retrograde. However, when existing in the rock in small amounts as a phosphate, the aluminum is supposed not to occasion a loss of phosphoric acid, both the hydrated and the non-hydrated phosphate being soluble in the precipitated condition in phosphoric acid.

Carbonates of calcium when existing in small quantities in phosphate rock, are beneficial rather than injurious. When the ground rock is treated with acid the carbonate is the first of the ingredients to be attacked, and the heat thus engendered promotes subsequent reactions among the other constituents. Moreover the carbon-dioxide gas given off from the carbonate, lightens the mixture and facilitates drying. Phosphate rock low in, or lacking carbonate develops little heat in mixing, and reacts slowly. In such cases this constituent must be added. It is true that the presence of the carbonate necessitates the use of an increased amount of acid, which in turn results in the formation of an increased amount of calcium sulphate

or gypsum. The amount of carbonate that is desirable is sometimes given as 5 per cent, but the limits are not strict, and the manufacturers do not as a rule find it necessary to specify directly the amount of the carbonate that the rock must or must not contain. Indirectly, however, an excess of the carbonate is guarded against by other requirements as to the grade of the rock. If it is true as elsewhere stated in this paper that the principal mineral of the massive phosphate deposits is a calcium carbonophosphate, this fact will afford an explanation of the presence of the desired amount of carbonate in all phosphate deposits of this class.

The fluorine found in phosphate rock, upon being attacked by the acid, form hydro fluoric acid gas which passes into the atmosphere, it being estimated that as much as from 50 to 66 $\frac{2}{3}$ per cent of the fluorine present is eliminated in this way. Although a small amount of acid is used up in this reaction and a proportionate amount of calcium sulphate formed, yet it is seldom, if ever, necessary to specify against the fluorine content of the rock, the amount present being negligible.

Among the numerous other impurities that may be present in phosphate rock, silica and clay are perhaps the most common. Here also should be mentioned moisture, which when present not only adds bulk to the shipment but also interferes with the processes of manufacture. The excess of moisture must, therefore, be removed by drying, not more than 3 or 4 per cent being allowable in the rock as shipped.

THE ORIGIN OF PHOSPHATE DEPOSITS.

The origin of phosphate deposits is such that the presence of associated minerals as well as constituent impurities is almost invariable. The original source of phosphorus, the constituent for which phosphate rock is mined, is in igneous and crystalline rocks, where it exists in combination with other elements forming phosphate minerals. These minerals, as indeed is true of all minerals, are soluble in water, the degree of solubility, however, varying with the different minerals, and with the diverse conditions to which they are subjected. Indeed some very interesting and suggestive observations have been made on the relative solubility of phosphates under varying conditions. Thus it has been shown that the solubility of the phosphate minerals is increased by the presence of decaying organic matter in water. They have also been found to be appreciably soluble in carbonated waters. In this connection Reese³ has made the very important observation that while the phosphate dissolves freely in waters containing decaying organic matter and in carbonated waters, yet when allowed to stand over calcium carbonate, the phosphate is redeposited. In summing up his observations Reese says: "This experiment shows that phosphates may be transported in hard waters, but on standing on calcareous beds would tend to be given up." In speaking of hard waters the author evidently has in mind, waters containing,

²J. Fritsch: *The Manufacture of Chemical Manures*, p. 79 (1911).

among other things, carbon dioxide in solution, and his conclusion is that such waters will or may drop the calcium phosphate from solution when they stand over limestone. These observations, if true, have two important corollaries, one of which has been noted by Clarke,⁴ namely, that in the presence of the carbonate, the phosphate would probably not be dissolved, while the carbonate could pass into solution, thus leaving the enriched residue of phosphate. The second corollary is that calcium phosphate taken into solution by the soil waters at and near the surface may be thrown out of solution in case the water stands for a time at a lower level in the earth on or over limestones. That this process may have been and probably was a factor in the formation of large phosphate deposits resting upon limestone will be shown in the subsequent pages of this paper.

The rain water in passing through the soil and surface materials receives organic acids from the decay of vegetable and animal matter. It also receives carbonic acid which is held in solution, the water thus becoming carbonated, and hence more efficient as a solvent. The original rocks and the soils derived from them contain particles of the phosphate minerals, which when acted upon by the ground waters pass slowly into solution. It is through the solution of the mineral, its removal and subsequent redeposition that workable phosphate deposits are formed. When it is remembered that the phosphorus in the igneous rocks amounted to merely a fractional part of 1 per cent of the whole,⁵ and was without doubt originally widely disseminated, the importance of the processes of concentration of the mineral by ground water and the extent to which they have operated becomes evident.

The removal of the mineral from the original rocks and its concentration in later rocks is by no means a simple process. There are as a rule many intermediate stages, the load being taken up, dropped again for a time, only to be once more started on its journey. Among the primary results of concentration and enrichment may be mentioned the phosphate deposits of the crystalline rocks, where the mineral is found in veins, being more or less perfectly crystallized as the mineral apatite. Of deposits of this class some, including those of Canada, are of economic importance, and would be more extensively worked were it not that other and more cheaply mined phosphate deposits are available.

Of the phosphate taken into solution by the ground water a part is taken up from the soils through the roots of plants, and thus becomes a constituent of the plant life of the earth. From the plants the phosphorus passes to plant-eating animals, and through them to carnivorous animals. Phosphorus thus be-

comes a constituent of the organic life of the earth. The bones of the vertebrate animals in particular contain an appreciable amount of calcium phosphate. It seems well established also that certain of the important phosphate deposits, as well as the guano deposits, are derived from excrement and remains of gregarious animals, particularly birds. It is also true that a part of the phosphate taken into solution by the ground waters is again thrown out owing to changed chemical conditions, and in this way important phosphate deposits are formed. In either case, however, the phosphate may be regarded as only temporarily delayed in its round of circulation. Ultimately phosphate is carried in solution in the ground waters through springs and rivers to the ocean. While the amount in solution at any one time is relatively small, yet through the continued operation of this agency over long periods of time, a large amount has reached the ocean.

The phosphate carried into the ocean is again removed from solution through the agency of organic life, or, owing to changed chemical conditions, is precipitated. Of the animals that utilize phosphorus taken from the sea water in the construction of a shell covering or skeleton, the best known perhaps is the brachiopod, *lingula*, the shell of a recent species of which has been found to contain 85.79 per cent of calcium phosphate. The tests of the crustacea, although less distinctly phosphatic than the shell of *lingula*, contain an appreciable amount of phosphate. Thus the shell of a recent lobster was found to contain 3.26 per cent of calcium phosphate, while the lobster as a whole contained 0.76 per cent.⁶ The aquatic plants also utilize some of the phosphorus in solution in the water and through them the phosphorus passes to the skeleton of vegetable-eating aquatic animals, and through them in turn to the carnivorous animals.

The phosphorus taken from solution by chemical action is evidently considerable, since nodules of chemical origin, high in phosphates, are found somewhat abundantly in the bed of the ocean. Some of these nodules, reported by Clarke,⁷ contain 19.96 to 23.54 per cent of phosphoric acid.

The amount of phosphate that finds its way into the sedimentary formations through organic and chemical agencies is thus undoubtedly considerable, resulting in the enrichment of certain deposits, which, if not workable, at least serve as an important source of phosphate from which by further concentration workable phosphate deposits are formed.

In this respect the deposition of calcium phosphate is analogous to that of the related mineral calcium carbonate, although of the carbonate much more extensive deposits accumulate than of the phosphate.

Silica (SiO_2) in its round of circulation in the earth presents some interesting analogies and yet strong

⁴American Journal of Science, 3d Series, vol. xliii, p. 402 (1892).

⁵Bulletin No. 330, U. S. Geological Survey, p. 443 (1908).

⁶According to Clarke, Bulletin 330, U. S. Geological Survey, p. 32 (1908) the amount of phosphorus in the lithosphere is 0.11 per cent.

⁷Bulletin 330, U. S. Geological Survey, p. 448 (1908).

⁸Bulletin 330, U. S. Geological Survey, p. 105 (1908).

contrasts to both calcium phosphate and calcium carbonate.

While the round of circulation of phosphate minerals is capable of demonstration as a normal process comparable to that of other common minerals, yet the actual processes of the accumulation of large workable deposits of phosphate rock are in many ways complicated.

FLORIDA PHOSPHATE DEPOSITS.

The complexity of origin of the phosphate rock and the manner in which impurities are included in the formation is well illustrated by the Florida phosphate deposits. Of these there are two distinct types, known respectively as the hard-rock and the land-pebble phosphates. These differ materially in their location, origin and manner of occurrence. The hard-rock phosphates lie in a belt along the Gulf side of the peninsula, extending in a general north and south direction roughly paralleling the Gulf coast for a distance of about 100 miles. The land-pebble phosphate deposits are found farther south, lying chiefly in Polk and Hillsboro counties.

The hard-rock phosphate deposits rest upon a thick and very pure, light-colored, porous and cavernous limestone known as the Vicksburg formation, which is of Lower Oligocene age. At present, in that section of the state no formation other than the phosphate itself lies on top of this limestone. It has, however, been demonstrated by the combined observations of several geologists that certain formations of which only a residue remains formerly extended across the area that now holds the hard-rock phosphate deposits. The formations referred to are Chattahoochee limestone and Alum Bluff sands, both of which are of Upper Oligocene age. These formations are now found bordering the hard-rock phosphate area. The proof of their former extent has been given elsewhere and need not be repeated at this time.⁶ The hard-rock phosphate deposits are made up largely of the residue of these formations which have disintegrated *in situ*, and accordingly consist of a mixture of materials of the most diverse character including sands, clays, limestone fragments, pebbles and water-worn flints, vertebrate, invertebrate and plant fossils; in fact a heterogeneous mixture of the relatively insoluble and resistant elements of the earlier formations.

The phosphate itself is derived from the Alum Bluff sands, the later and thicker of the two formations that have disintegrated. This formation, the Alum Bluff, in some places reaches a thickness of several hundred feet, and has a large areal extent reaching from west Florida, through northern and central Florida, into southern Florida. Throughout its entire thickness, and throughout its whole areal extent this formation is distinctly phosphatic, although in no instance is the

phosphate in this formation sufficiently concentrated to form workable deposits.

While these formations, the Chattahoochee and the Alum Bluff, were disintegrating in the area that is now the hard-rock phosphate region, the calcium phosphate from the Alum Bluff formation was gradually being taken into solution by ground water and was being redeposited at a lower level in the earth, thus forming the workable hard-rock phosphate deposits. In this process the replacement of the original limestone by calcium phosphate was an important factor, and these deposits afford excellent illustration of the formation of phosphate rock by the replacement process, the shells of the original limestone in many instances retaining their form, although changed chemically to calcium phosphate. In addition to replacement, other processes are observed, prominent among which is the formation of the phosphate by precipitation from solution in a manner similar to the formation of calcium carbonate deposits in caves. This process is evidently secondary, and being now operative is to be observed in the phosphate boulders themselves, in which all existing cavities are being gradually filled by the accumulation of calcium phosphate. By this process pinnacles are formed hanging from the roof of the cavities, while successive layers of phosphate are spread out over the floor of the cavities. This method of the formation of phosphate deposits has given rise to very high-grade phosphate rock, the Florida hard rock grading, under present methods of mining, 77 to 80 per cent tricalcium phosphate, while individual specimens contain 84 to 85 per cent.

While the origin of the hard-rock phosphate in its present form is thus clearly evident, there yet remains a large field of investigation to determine the chemical processes by which the phosphate is first taken into solution, and is subsequently redeposited. Some of these processes, however, are well understood. That normal phosphate is to some extent soluble in soil waters is well established and fully recognized. In the hard-rock phosphate section of Florida there is practically no surface drainage, the rain water passing directly into the earth. At a lower level the circulation of the water is interfered with and the water may become stationary or nearly so. The check in circulation is due in some instances to masses and beds of clay residual from disintegrating formations. In any case the movement of the water is checked upon reaching the water line. The relation of the phosphate deposits to the ground-water level, and also the evident and probable changes of the water level during geologic time have been discussed in the writer's paper on these deposits previously referred to. While the processes that brought about the deposition of the phosphate may not be fully understood, yet it is apparent that there are important changes in the chemical conditions. Among these may be mentioned the check to the free movement of the water, and the evident ming-

⁶Origin of the Hard Rock Phosphate Deposits of Florida, by E. H. Sellards, Fifth Annual Report, Florida State Geological Survey, pp. 23-80 (1913).

ling at this depth of different waters. In this connection the observations of Reese, previously referred to, in which it is shown that calcium phosphate in solution in carbonated waters is precipitated when the water stands over limestone, are particularly suggestive. As shown in my earlier papers the hard-rock phosphates of Florida are invariably formed directly upon limestone, and need not be sought for elsewhere. Moreover they are thrown out of solution from carbonated waters which pass over and through these limestones, the manner of their formation apparently being entirely in accord with Reese's experiments.

The land-pebble phosphate deposits of Florida are probably derived, like the hard-rock deposits, from the Alum Bluff formation. The processes by which they have accumulated in their present form are, however, strikingly different. The hard-rock phosphates, as has been stated, represent chemical precipitates or replacement deposits, the phosphate having been transported to its present location in solution. The land-pebble deposits, on the other hand, appear to represent materials which are residual from erosion of the parent formation. The hard-rock phosphates occur in sections where the parent formation has entirely disintegrated over limestones. The land-pebble deposits on the contrary are found as a blanket deposit resting upon, and representing a concentration from, the parent formation. The matrix of the land-pebble deposits is, therefore, not strikingly different from that of the hard-rock deposits except as chemical action has modified the residue, particularly by the formation in many instances of siliceous boulders in the hard-rock deposits.

The grade of rock produced from the land-pebble deposits under the present methods of mining varies from 66 to 74 per cent tricalcium phosphate, while individual samples contain 77 to 78 per cent.

TENNESSEE PHOSPHATE DEPOSITS.

As further evidence of the complexity of the origin of phosphates in workable deposits, and of the diversity of ways in which they accumulate, may be mentioned the phosphates of Tennessee. Several distinct types of phosphate are found in Tennessee, only two of which, however, are being mined at present, namely, the blue rock and the brown rock. The blue phosphate occurs as a bedded deposit within, but forming the lowest member of the Chattanooga formation of Devonian age, which rests directly upon limestones of Ordovician age. The beds vary in thickness from zero to 50 in., although the bed of high-grade rock rarely exceeds 20 in. in thickness. In grade the blue rock varies from 30 to 85 per cent. The iron and aluminum in the better grade aggregate less than 3 per cent. The brown-rock phosphates, which at present are being more extensively mined than the blue, occur in irregular deposits lying near the surface and resting upon limestones. The brown rock is largely a shelly rock which breaks up into pieces of varying size. In addition, however, there is considerable proportion of small

pebbles which in mass have a dark brown color. The underlying limestone has an irregular top surface, and not infrequently projects into the phosphate stratum. The limestone is dense and has a bluish cast. It is more or less phosphatic. The age of this underlying limestone is Ordovician. The overburden consists of clay, some phosphate and a limited amount of sand. It is reddish in color, and in thickness is entirely variable, averaging perhaps 8 or 10 ft.

The brown phosphates of Tennessee are very evidently formed *in situ* from phosphatic limestone. Hayes and Ulrich⁹ find that at least four limestone horizons have given rise to brown phosphates in Tennessee. The calcium carbonate from the limestone is more or less completely leached out, and is replaced in part at least by calcium phosphate.¹⁰ The rock is thus enriched and becomes a workable phosphate. The leaching of the rock usually begins along jointing planes and unchanged masses of the original limestone in this type of deposit frequently remain as "horses." Two types of deposits are recognized, which are described as blanket and collar deposits. The blanket deposits are those which extend over a considerable area. The collar deposits are formed where the phosphatic limestone comes to the surface around the slope of a hill. The collar deposits are necessarily limited in extent, while the blanket deposits may cover considerable areas. The brown phosphates, from their manner of origin, have necessarily accumulated in comparatively recent times.

The blue phosphates, on the other hand, are much older than the brown, having accumulated in their present form during Devonian time. It is believed by Hayes and Ulrich that the blue phosphates were originally formed as residual material from, and resting upon, the Ordovician phosphatic limestones, much as the brown phosphates of the present time are formed. After this residual material accumulated the area was depressed allowing the sea to cover the limestone. By the action of the waves in shallow water the residual mass was pretty thoroughly washed, the soil and clay material being sifted out and carried away while the phosphatic material was left to form the phosphate rock as found at present. The sea subsequently deepened, so that shales and other formations were deposited upon the phosphate.

The richest of the blue-rock deposits is believed to have been formed from the Ordovician limestone, known as the Leipers formation. This formation is full of the same minute spiral and other shells that occur abundantly in the immediately overlying phosphate rock. Phosphates were formed from Ordovician limestone other than the Leipers formation, but they are of a lower grade and at present are not workable.

It would thus seem that the blue rock of Tennessee

⁹Columbia Folio, U. S. Geological Survey, p. 5 (1903).

¹⁰Some of the brown phosphate of Tennessee is formed, according to Dr. A. F. Rogers, by replacement of crinoidal limestone by calcium phosphate. (Personal letter, April 1, 1914.)

was formed during the interval between the Ordovician and the Devonian, washed during the Devonian, and in this condition was preserved for modern mining operations.

WESTERN PHOSPHATE DEPOSITS.

The extensive phosphate deposits of the western United States are interbedded with sedimentary formations, and to this extent resemble the blue-rock phosphates of Tennessee. The rock in these deposits is described as prevailing oolitic, although an exceptional occurrence is recorded by Richard and Mansfield¹¹ in which high-grade rock was found to consist of shell fragments regarded by Girty as broken shells of pelecypods. The source of the phosphoric acid and the history of its accumulation in the form in which it is now found in these deposits, if at present obscure, will perhaps, upon further investigation, become apparent.

PHOSPHATE DEPOSITS FROM GUANO.

The phosphate deposits of Navassa, a small island in the West Indies, may be mentioned as an illustration of those which are believed to have been formed from guano. In the case of phosphate deposits formed from guano, the phosphate is taken in solution by rain water, and after being carried to a lower level is re-deposited, replacing the carbonate of the limestone. The rapidity with which this process may be carried on is illustrated by an instance cited by Dr. Albert R. Ledoux¹² in which limestone on one of the south Pacific islands was observed to have been changed to phosphate to a depth of several feet within a period of 20 years, the phosphoric acid in this instance being leached by rain water from recently deposited guano.

MINING.

Phosphate rock is mined either by open-pit or by underground mining. Those deposits having a removable overburden are mined by the open-pit method, underground mining being resorted to only for deposits interstratified with other formations, so that the overburden cannot be removed.

Underground Mining.—The deposits mined in America by underground mining include the blue rock of Tennessee, the Arkansas deposits, and for the most part the extensive deposits of the western United States, which are as yet but little developed. In underground mining, ordinarily, operations begin at the surface outcrop of the phosphate stratum, the first rock being uncovered by stripping off the overburden. When the overburden can no longer be removed economically, drifts are run into the bank and the phosphate rock removed, support being given to the roof, when necessary, after the phosphate is taken out. This method of mining is similar to that used in mining coal seams. In the Arkansas and Tennessee mines the phosphate rock is first drilled and blasted. It is

then broken up by pick and loaded into tram cars to be drawn from the mine.

Open-Pit Mining.—By far the greater part of the phosphate rock produced in America is obtained at present by open-pit mining, in which the overburden is first removed from the rock. The purity of the rock, however, is not materially affected by the methods employed in removing the overburden, and hence it is not necessary to describe these methods in detail. It may be noted, however, that diverse methods prevail, depending upon the thickness and character of the overburden, the magnitude of the operations and the facilities available. Examples may still be found of removal of overburden by pick and shovel, team and scraper, or team and dump cart. It is, however, only a shallow overburden that can be so removed profitably. In the larger mining operations the overburden is removed by steam shovel, by means of which the material is loaded into cars, which are then drawn to the overburden dump; or the overburden is removed by the hydraulic method, the material being pumped through pipe lines to the overburden dump. Whatever method is employed a limited amount of burden remains with the phosphate rock which must be separated in subsequent treatment.

It is not necessary in this connection to describe in detail the methods of removing phosphate rock from the pit, since the purity of the rock is but incidentally affected thereby. It may be said, however, that the phosphate rock is either loaded by pick and shovel on wagons or tram cars to be drawn from the pit, or it is taken up by dredge or by hydraulicking. If taken up by the hydraulic method the rock is forced through pipe lines to the washer plant. The character of the deposit determines the methods of removal that may be employed. Where the phosphate is loaded by pick and shovel, such objectionable impurities as siliceous boulders, limestone rock and clay balls are rejected at the pit, and in some mines only the coarse rock is taken, leaving the finer phosphate, clay and sand.

As a rule, however, there is no attempt to separate the phosphate from the matrix before removal from the pit.

PREPARATION OF PHOSPHATE FOR MARKET.

The phosphate rock mined by the open-pit method must be washed and dried. The methods of treatment described in this paper are those followed in America and particularly in the Florida mines.

Washington.—The hard-rock phosphate of Florida when brought from the pit is dumped on the grizzlies with 2- or 2½-in. openings. The fine materials of the matrix pass through while the coarse materials, including phosphate, flint, and limestone boulders, and clay balls, are lodged on the grating. The phosphate boulders are then thrown by hand into a rock crusher near by, while the flint and limestone boulders and clay balls are discarded. That part of the matrix which passes the grizzly together with the rock from the crusher is dropped into a log washer beneath. The

¹¹Bulletin 470, U. S. Geological Survey, p. 376 (1911).

¹²Transactions of the N. Y. Academy of Science, vol. ix, p. 85 (1890).

practice in the land-pebble mines is somewhat different from that followed in the hard-rock section, the matrix, as pumped from the pit, being thrown as a rule into a large revolving tube, known as a separator, punched "hit and miss" with holes 1 or 2 in. in diameter. As the separator revolves the phosphate pebble, as well as the finer materials of the matrix, fall through the openings and lodge on a screen beneath, while the coarser materials, including sand, rock and clay balls remain in the separator from which they are carried to the waste dump. From the screen beneath the separator the phosphate rock passes into the log washer. While this is the usual arrangement in the land-pebble phosphate mines, yet in some of the newer plants it has been found practicable to omit the separator altogether, the rock from the dump being allowed to enter the log washer after passing over a screen of about 1/16-in. mesh. When the separator is omitted practically all the matrix from the pit passes through the log washers, and it has usually been found necessary in these plants, to install a crusher, which is then placed between the two logs. The larger pieces of bone and phosphate rock, as well as the clay balls, if not disintegrated by the washer, are broken up in the crusher, and the phosphate which they contain is saved.

The log washer, through which the phosphate rock is passed, consists of two cylinders or logs placed side by side in a box or trough. A series of blades arranged in a spiral is fastened to each cylinder. The trough is inclined, the phosphate being run in at the lower end, and as the logs are made to revolve in opposite directions, the phosphate rock is pushed forward by the blades, meeting as it goes a constant stream of water. By this means the rock is pretty thoroughly washed, the water carrying all the finer materials of the matrix escaping at the lower end or in the newer washers through an opening at the side of the trough. Frequently the phosphate rock is passed through a second log of the same type as the first, and in all cases receives a final rinsing while passing over screens.

In the hard-rock phosphate mines of Florida the coarse phosphate after leaving the rinser is made to pass over a picker belt which is usually made in the form of a large revolving table. The phosphate rock remains on the picker belt during one complete revolution of the table being carefully inspected by men and boys stationed around the table. The inferior rock, clay balls, flint and limestone fragments, so far as recognized, are picked out and discarded at this time, thus bringing up the grade of the shipment. In the land-pebble mines the phosphate rock from the last washer falls on jig screens, the finer of which are 3/64 or 1/32 in. mesh. From these screens the rock is elevated by endless cup chains to the loading bin.

Drying.—After being taken from the pit the phosphate rock must be dried before being marketed. Two methods of drying are in use. The first of these,

which is adapted to drying coarse rock, consists in piling the phosphate rock on ricks of wood. The wood is then burned, thus drying the rock. This method assists somewhat in cleaning, since clay and sand adhering to the rock, tend, after drying, to loosen and fall away in subsequent handling.

The second method of drying, which is now largely used, is by the use of heated rotary cylinders through which the rock is passed. The rock is introduced usually at the cool end of the cylinder, and by means of various devices is made to pass through, escaping at the furnace or heated end. This method is adapted to drying small pebble rock; the coarser rock must be crushed before being dried by this method.

IMPROVEMENTS IN MINING METHODS.

An important factor in the cost of producing phosphate rock is the necessity of discarding the low-grade rock, as well as that which cannot be properly cleaned or separated from the minerals with which it is associated. It is encouraging, however, to find that through improved methods of mining the amount of phosphate thus discarded is being considerably reduced, while the grade of rock produced is being maintained or advanced. In the modern phosphate-mining plants of Florida, practically no phosphate rock reaches the dump except that which will pass a 1/16, 3/64 or 1/32-in. mesh screen, or is carried out with the overflow from the side opening in the log washer. In Tennessee, where a very considerable part of the brown-rock phosphate is in the form of minute pebbles, settling tanks for saving the small pebble have been introduced in late years. From the log washer the fine material passes through these tanks, and much phosphate that was originally thrown into the dump is thus cleaned and saved, and in fact some of the abandoned dumps in Tennessee are now being rewashed by this method.

However, notwithstanding these improvements in mining methods a very considerable amount of phosphoric acid in the form of very fine pebble and soft phosphate still finds its way into the waste dump. It is true that a large part of the phosphate that is thus lost is too high in iron and aluminum to be used in the manufacture of fertilizers under existing processes. It is, however, none the less desirable that the phosphoric acid be saved. To this end it is to be hoped that devices for recovering the very fine pebble phosphate may be further perfected, and that a new process of manufacture may be developed in which the grade of rock that can be used is not so strictly limited.

Switzerland produces no coal and depends entirely upon Germany for its supply, with relatively small quantities from Belgium and France. The total import during the calendar year 1913 was: Anthracite, approximately 2,000,000 tons, valued at \$12,000,000; coke, 439,000 tons, valued at \$3,600,000; briquets, 968,530 tons, valued at \$5,600,000.

SEARCH FOR POTASH IN TEXAS.*

The University of Texas, Austin, Texas, has just issued a bulletin, written by J. A. Uddan, geologist of the Bureau of Economic Geology and Technology. The bulletin states that, while this paper describes the section of a single boring, it really gives the only facts so far known concerning the deep stratigraphy of a region covering one-fifth of the area of the state.

The deepest boring in Texas is now at Spur, in Dickens County, south of the east portion of the Panhandle. This boring has been made by S. M. Swenson & Sons, large landholders in this and adjoining counties, in search of water for the town of Spur and as a general exploration of the formations for the vicinity. Spur is the present northwest terminus of the Stamford & Northwestern Railway.

What may eventually be the most important economic result of this boring is that it has proved the existence in the dolomite beds of a stratum, or horizon, from which comes a water sufficiently rich in potash to hold out inducements to prospective search for this mineral.

The presence of much anhydrite and salt in the uppermost 1,200 ft., in the section of the boring, caused the writer to suggest that an analysis of the water in the well be made to determine its potash content. At the time this suggestion was made the hole had already been cased to below 1,300 ft., and all water from strata above this depth had been shut off.

A sample of water was taken on April 12, 1912, after the water had been bailed out down to 2,200 ft. below the surface. This water was analyzed a week later by S. H. Worrell, chemist of the Bureau of Economic Geology and Technology of the University of Texas. His analysis showed the following mineral ingredients present in the quantities stated:

	Grains per U. S. gal.
Calcium sulphate	1,406.19
Calcium chloride	679.02
Magnesium chloride	219.20
Sodium chloride	3,410.55
Potassium chloride	324.14
	6,039.10

In other words, the potassium chloride amounted to 5 grams per liter, and constituted 5.4 per cent of all solids. This being an unusually high content of potash in natural water, arrangements were later made for taking samples of water from different depths below the bottom of the 1,350-ft. casing. In June of the same year 14 such samples were obtained and later tested for potash. The depths at which these samples were taken and the determined contents of potash in each are given in Table I, in which the April sample is included also.

Some of the samples were taken before much water had been bailed out of the well, while other samples were taken at intervals as the water was being bailed out. The table shows these particulars of the sam-

pling, and it also gives some data on temperatures of the water samples when coming out of the well. The fact that the samples from 2,200, 2,600 and 3,000 ft. below the surface, bailed out when the water was standing at 1,500 ft. below the surface, had in each case a lower temperature than the samples taken at 2,690, 2,400 and 2,300, when the water was standing at considerably lower depths, respectively, 2,600, 2,400 and 2,300 ft. below the surface, shows conclusively that the water from the different depths in the well had been mixed by convection currents caused by differences in temperature in the upper and the lower part of the hole. Each one of these analyses, hence, shows the potash content of a sample of water containing a mixture of all soluble substances present anywhere in the wall of the well. It is not at all likely that the potash is uniformly distributed in this section of sediments 2,650 ft. thick. On the contrary, it can be taken for granted that the mineral is confined to one

TABLE I—POTASH CONTENT OF FIFTEEN SAMPLES OF WATER TAKEN AT DIFFERENT DEPTHS IN S. M. SWENSON & SONS' DEEP BORING AT SPUR, TEXAS.

	A	B	C	D	E
1.....	800	800	72.2	.5	?
2.....	1,360	300	59.1	.3	?
3.....	1,390	1,390	61.9	.4	?
4.....	1,500 (Drip water)	1,550	21.4	.4	?
5.....	1,600	1,600	42.9	.2	71
6.....	1,800	1,390	94.4	.4	?
7.....	1,830	1,830	47.2	.2	?
8.....	2,000	2,000	41.0	.2	?
9.....	2,200 (April sample)	2,200	324.1	5.4	?
10.....	2,200	1,500	113.3	.5	71
11.....	2,300	2,300	60.2	.3	74
12.....	2,400	2,400	69.6	.4	73
13.....	2,600	1,500	86.2	.4	71
14.....	2,690	2,400	29.1	.2	75
15.....	3,000	1,500	43.6	.2	73

A—Depth at which sample was taken, in feet, below surface.

B—Depth of water when sample was taken, in feet, below surface.

C—Grains of potassium chloride per U. S. gallon.

D—Per cent of total solids.

E—Temperature of sample when taken, Fahr.

or, at most, to a few distinct beds produced at times favorable to the precipitation of this mineral in the sea in which the sediments formed, or introduced by ground water at some later time.

As the convection of the water in the well is slow, owing to the small size of the hole and the slight difference between bottom and top temperatures, it is to be inferred that an ingredient in the solution supplied at a certain level would be present near that depth in greater quantity than at any other depth.

The differences in the analyses made, hence, indicate the presence of a potash-bearing stratum somewhere near 2,200 ft. below the surface in this well. The sample having 324.1 grains per U. S. gallon was taken when work on the well ceased for a while, in April, 1912. All the other samples were taken two months later, before the work of drilling was resumed. The water had then been standing undisturbed for two months, and the potash-bearing ingredient in the entire seepage had evidently been more evenly distributed through all the water in the hole. The maximum

*From The American Fertilizer.

quantity of potash in the 14 samples taken in June is only one-third the quantity in the sample taken in April. It has been suggested that the general tendency of potash to diffuse by capillarity might readily account for the lesser amount present at 2,200 ft. after the well had been left underdisturbed for two months. The potash would tend to "soak" into the walls of the hole, and be thus extracted from the solution by capillary filtration. But we still find the greatest quantity of potash (113.3 grains) at the depth where the first sample was taken containing 324 grains per U. S. gallon. It is also quite significant that the sample showing the smallest quantity of potash was the only sample not really a mixture of all the water in the well. This was taken by suspending the bucket at 1,500 ft. when the water had been bailed down to 1,550 ft. It consisted of water dripping from the wall of the hole, and probably was a mixture of spilled water adhering to the wall of the well, and of some water trickling out from the rock above the depth where the bailer was hung, below the base of the casing. This sample contained only 21.4 grains of potash per gallon.*

Wishing to verify, if possible, the evidence from the water analyses, a number of tests for potash were made on the rock samples. It was evident that the chances for finding the original potash in the samples was very small, for two reasons. In the first place, the samples taken at the indicated level were few and were selected to represent the principal kinds of rock. Only one single sample was taken to represent all the material penetrated from 2,128 to 2,212 ft. This was a brown sandy clay. Should this bed contain the potash, it would most likely be confined to a few feet of the deposit rather than be present in the whole stratum. The sample taken from this bed consisted of fairly large cuttings, and, no doubt, really represented but a few feet of the whole bed. Another sample represents 42 ft. of rock, of nearly the same kind, from 2,068 to 2,110 ft.

It is worth while to note that the samples from 2,000 to 2,300 ft. were taken during the time from May to September, 1911. There was then no thought of looking for potash. The first test for potash in the water was made in April of the following year. The analyses of the rock samples from 732 to 1,250 ft. were made in February, 1914. All analyses were made by the chemist of the Bureau, S. H. Worrell. The results are given in Table II.

It can hardly be a mere coincidence that traces of potash were found in the solid rock only near the level where the potash content was highest in the well water. The very unusual amount of 324 grains per gallon also strongly suggests the existence of more than a mere slight impregnation in some stratum. Even after the potash had dissolved from the exposed walls

of this stratum, and had been diluted through a column of water 3,000 ft. high, it was present in an amount averaging 60 grains per gallon for all the water in the well. It is to be recalled that salt was present in some rock samples, evidently as an original ingredient, from 1,600 ft., and again from 2,244 to 2,264 ft. below the surface.

Considering the great value of a workable deposit of potash, it seems worth the while to call attention to another circumstance in connection with these observations. In either direction north or south from Spur the formations lie practically horizontal for at least a hundred miles, and the potash-bearing horizon, whether it be such or not in other places, must be at about the same depth as here, in these directions. It seems to the writer that the general conditions indicated in this boring, the existence of great salt beds

TABLE II—TESTS FOR POTASH IN CUTTINGS AND PIECES OF CORE FROM THE SPUR BORINGS.

Depth of samples in feet below surface.		Potash.
From—	To—	
732	741 (cuttings)	0
914	931 (core)	0
931	932 (core)	0
958	962 (core)	0
962	1,113 (core)	0
1,113	1,117 (core)	0
1,117	1,123 (core)	0
1,174	1,222 (cuttings)	0
1,222	1,235 (core)	0
1,235	1,250 (core)	0
Near	2,000 (cuttings)	0
	2,200 (cuttings)	0
	2,042	2,047 (cuttings) Trace
	2,047	2,049 (cuttings) 0
	2,049	2,063 (cuttings) 0
	2,064	2,068 (cuttings) 0
	2,068	2,110 (cuttings) Pronounced trace
	2,110	2,126 (cuttings) 0
	2,128	2,212 (cuttings) 0
	2,212	2,214 (cuttings) 0
	2,214	2,219 (cuttings) 0
	2,219	2,241 (cuttings) 9
	2,244	2,264 (core) 0
	2,271	2,329 (cuttings) 0
	2,329	2,331 (cuttings) 0
	2,331	2,336 (cuttings) 0
	2,336	2,338 (cuttings) 0
	2,392	2,394 (cuttings) 0

and beds of anhydrite, together with the proven potash-bearing stratum, warrants an examination for potash in water from the same horizon in any boring made in this territory.

East or west from Spur the depth to this horizon will be greater westward and less eastward. The elevation of the railroad depot at Spur is 2,274 ft. above sea level. This is 666 ft. higher than the elevation at Cisco, about 120 miles to the east-southeast. A line connecting these two points may be taken to follow the direction of the general dip of the formations to the west. The bottom of the well may be taken to represent the beds out-cropping at Cisco. On this assumption, the general dip between Cisco and Spur, a distance of 120 miles, will be equal to the depth of the Spur well, less the difference in elevation of the two places. This gives us a dip to the west of nearly 32

*The above account of the writer's observations on potash are taken, with slight changes, from his article on "Potash in the Permian of Texas," published in The American Fertilizer for December 14, 1912.

ft. per mile. Our inability to fix the precise level in the Cisco formation reached in the boring may make this figure either a little too high or too low, but it cannot be far from right. Taking into consideration the general east slope of the land surface, which averages 6 ft. per mile, any stratum should come near the surface at the rate of 38 ft. per mile eastward from Spur.

Assuming, now, that this general dip is constant between the two points, and that the formations are continuous, the horizon which yielded potash in the Spur well should outcrop in a belt where the land surface intersects the dipping plane lying 2,200 ft. below the surface at Spur. This belt would extend through Haskell and Jones Counties. It is not to be expected that potash should be found in any outcropping rock in this belt, owing to surface leaching, but well waters there might show its former existence. Dr. Harper and Dr. Bailey, of the School of Chemistry in the University of Texas, have analyzed a number of water samples from wells near Haskell, and they have informed the writer that some of these waters contain an unusually large quantity of nitrate, which is not believed to be derived from the surface. It is suspected that this nitrate exists in the form of a potassium compound, as saltpeter. Along the line of the Kansas City & Orient Railroad in these counties the potash-bearing horizon may be looked for at depths of from 100 to 400 ft.

For making a comparison between the Spur well-water and other well-waters in the Pennsylvanian and Permian formations of the north and central parts of Texas, the records of water analyses made by the School of Chemistry in the University of Texas have been examined. Seventeen analyses were found in which determination of potash have been made. All these have less than 8 grains per gallon, and average 2.16 grains per gallon. The records do not show what waters these were, in all cases, but they are all believed to have been well-waters.

TABLE SHOWING POTASH CONTENTS IN SEVENTEEN SAMPLES OF (WELL?) WATER FROM THE PENNSYLVANIAN AND THE PERMIAN FORMATIONS IN THE NORTHWEST AND CENTRAL PARTS OF TEXAS.

	Potash in Grains per U. S. Gallon
1. Weatherford, Parker County, well 215 ft. deep	.09
2. Haskell, Haskell County	.30
3. Weatherford, Parker County, well 1,425 ft. deep	.33
4. Arlington, Tarrant County	.52
5. Weatherford, Parker County	.61
6. Rochelle, McCulloch County	1.11
7. Mineral Wells, Palo Pinto County	1.21
8. Mangum, Eastland County	1.22
9. Burleson, Johnson County	1.39
10. Fort Worth, Tarrant County	1.40
11. Crazy Well No. 2, Mineral Wells, Palo Pinto County	2.45
12. Mineral Wells, Palo Pinto County	2.55
13. Thurber, Erath County	3.20
14. Lampasas, Lampasas County	4.34
15. De Leon, Comanche County	6.67
16. Mineral Wells, Palo Pinto County	7.52
17. Crazy Well No. 2, Mineral Wells, Palo Pinto County	8.03

RADIUM IN INDIA.*

Mr. M. C. A. Crump, of Bombay, who has been on a tour of the Provinces of Bihar and Orissa, in North-eastern India, to collect mammals for the Bombay Natural History Society, has written to local papers of a visit to the Singar estate in the Gaya district, where he was surprised to find that mining for pitchblende, which is the chief source of radium, had been started. He states:

Through the courtesy of the lessees I was permitted to visit the mine on Abraki Pahar, a small hill situated about half a mile due east of the village of Bhanekhap, which is being worked just now. It is only 42 ft. deep, as without aid of any mechanical contrivances progress is necessarily slow. In spite of these difficulties, however, over 8 hundredweight (1 hundredweight=112 pounds) of pitchblende has been won and there is every prospect of finding further segregations at a depth yielding a richer supply of the precious mineral. The concession was obtained in March, last, and covers a large area, but practically no prospecting has yet been done, except at Abraki Pahar, although outcrops of triplite (a ferrous manganous fluophosphate that seems to be associated with pitchblende) have been found in other parts of the estate.

Regarding Mr. Crump's investigations, the Times of India states:

Both pitchblende and uranium ochre have been known for many years to occur in the Gaya district at the Singar mica mines, though very little serious attempt has been made to ascertain the amount available. The records of the Geological Survey of India contain an account of the examinations of Mr. B. C. Burton of the workings.

From his report it seems that the pitchblende occurs in a pegmatite, which crops out on a hill known as Abraki Pahar lying due east of Bhanekhap and rising 200 feet above the surrounding alluvium. The pegmatite has a maximum width of 40 yards and is exposed above the alluvium for a distance of approximately 350 yards in a direction east 20° south. It is intrusive along the bedding of fairly coarse-grained muscovite schists dipping at between 30 and 50° north, masses of the schist being also caught up in the body of the pegmatite. At the junction between the pegmatite and the schists the latter contain tourmaline crystals in large quantity. This pegmatite has been mined for many years as a source of mica; before mining for pitchblende commenced the only indication of uranium on the surface consisted of small amounts of light yellow uranium ochre associated with triplite; but as the pits were deepened nodules of pure pitchblende were met with.

The pitchblende occurs as rounded nodules distributed throughout certain basic segregations in the pegmatite, which are several feet in diameter. In these basic segregations the following minerals occur, but not always together: White and yellow mica, triplite, ilmenite, tourmaline, pitchblende, and uranium ochre; while columbite, zircon, and torbernite have also been recorded.

Although the most important milk product in India is ghee, or clarified butter, obtained chiefly from the milk of buffaloes, yet for butter itself, which is the first stage in the manufacture of ghee, there is a considerable demand, owing probably to the difficulty of obtaining pure ghee. In manufacturing ghee it is sterilized so that it keeps for long periods, and is thus more suitable than butter for the hot climate of India. However, it is so much adulterated with fats and oils and is so difficult to obtain pure that the European element, at least, prefers butter.

*From Daily Consular and Trade Reports.

METALLURGY

THE COMMERCIAL CLASSIFICATION OF REFINED COPPER.*

By LAWRENCE ADDICKS.

Any adequate classification of a material of commerce such as copper must take into account both the limitations of the metallurgical processes by which the material has been obtained and the needs of the manufacturing processes in which it is to be employed. The metallurgical methods depend in turn upon the nature of the ores or other sources of supply and the manufacturing ones upon the ultimate uses of the finished product.

The world's copper supply comes from four main sources, sulphide ores, oxidized ores, native ores and scrap. Perhaps the chief chemical characteristic of copper is its affinity for sulphur and the largest deposits of copper ores consist of more or less complex sulphides. Near the surface these ores are frequently altered to oxides and carbonates by atmospheric influence and there are also large deposits entirely free from sulphur. Native copper ores where the copper exists as free metal occur in various parts of the world in small quantities, but notably in the enormous deposits in the northern peninsula of Michigan, where they form the source of the so-called Lake Copper.

Metallurgically there are three typical processes for producing crude or unrefined copper from the ore, based on the general principles of oxidizing sulphides and reducing oxides, (a) roasting, smelting and converting, (b) alternate oxidation and reduction and (c) direct reduction of oxidized ores. (a) which is a strongly oxidizing process by which the great majority of the American production is made from sulphide ores, results in the almost complete elimination of impurities which have volatile oxides, including some of the worst enemies of refined copper, such as arsenic. Converter bar nearly always runs 99 per cent copper plus silver and is not likely to carry more than a few hundredths of a per cent of any impurity but nickel. (b) is the old Welsh process, still used to some extent abroad, based upon the reaction between copper oxides and sulphides to eliminate sulphur as sulphur dioxide gas and carried out in a long series of roasts and fusions in reverberatory furnaces. The removal of impurities is here imperfect although they may be to a certain extent segregated in a portion of the product, when the origin of the "Best Selected" copper of Great Britain. When the ores are wholly oxidized the copper may be recovered by direct reduction in a blast

furnace (c) and as this is a strictly reducing process the resulting black copper seldom runs over 96 per cent, due to iron and other impurities reduced. Except in the case of "Best Selected" and similar English coppers, all of the products from the foregoing processes are given a further treatment or refining, which may be broadly divided into furnace or fire refining and electrolytic refining.

Fire refining is based upon the scorifying effect of cuprous oxide upon base metals contained in a bath of molten copper. The crude copper is melted in a reverberatory furnace and air blown into the bath. Cuprous oxide rapidly forms and dissolves in the bath, the blowing being stopped at or before the saturation point. In this way oxygen is carried to all parts of the molten bath and when there are any metals present which are more easily oxidized than copper, cuprous oxide is reduced back to copper and the oxide of the impurity is formed. If this oxide is not soluble in the molten copper it will float to the surface where it may be removed by skimming. As copper stands high among metals in the order of nobility the metallic impurities with the exception of the precious metals may be readily removed in theory. In practice while elimination proceeds rapidly while considerable quantities of impurities are present, the rate diminishes until traces are reached which cannot be slagged off with any reasonable amount of scorifying. Therefore furnace refining is limited in its application to relatively pure crude copper unless a low grade refined copper is contemplated. Less than ten dollars' worth of silver and gold per ton will justify electrolytic refining.

Returning to the bath of molten copper which has been skimmed clean, it is necessary to reduce the excess cuprous oxide dissolved, and no better way has yet been devised than the old Welsh process of covering the bath with a protecting layer of charcoal or low sulphur coke and then forcing the butts of green trees or poles of hardwood beneath the surface by means of suitable tackle. The cuprous oxide is reduced in this way until a normal amount corresponding to an oxygen content of from 0.04 to 0.07 per cent is left when the copper develops its best physical characteristics, the condition of the copper being followed by the appearance of the fracture of small buttons cast in a spoon or "say ladle" which is a sort of ductility test and by the swell or depression of the surface of an ingot as it cools, which indicates the gas content. The copper is then cast by means of one of the several types of ladling machines which have been very successfully developed in recent years.

*Paper presented at the annual meeting of the American Institute of Metals, Sept. 7-11, 1914, at Chicago, Ill.

When the copper is to be electrolytically refined it is first given a rough furnace refining and cast into anode plates, which are then electrolyzed in a strongly acid solution of copper sulphate. The same order of nobility applies, but the great preponderance of copper over the impurities is now an aid as it assists the selective action of the current in depositing only copper at the cathode. Silver and gold are also saved as they are insoluble in the electrolyte chosen and fall to the bottom of the tank as anode mud or slimes to be separately refined and parted. It is quite evident that copper entering an electrolytic refinery must entirely lose its identity and that the purity of the resulting cathode copper will depend upon the conditions under which electrolysis is carried out rather than upon the momentary quality of the day's anodes. Therefore it is not necessary to consider whether the input be converter bar, black copper or Lake mineral when buying electrolytic, but simply whether the product meets the accepted standards of quality for electrolytic copper.

Electrolytic cathodes should be very pure. They generally run about 99.95 per cent copper, much of the missing 0.05 per cent probably being hydrogen. The metallic impurities generally total about 0.02 per cent. Except for the fact that individual cathodes may vary more or less in impurity content they are ideal material for brass making. Copper producers, however, have never encouraged the sale of cathodes, as there is apt to be some shrinkage in weight during shipment owing to the comparative ease with which nodules or small pieces can be detached either accidentally or intentionally. Also cathode shipments unbalance the work in a refinery in proportion to their magnitude, as melting cathodes into market shapes is a distinct part of the process.

This melting is done in a reverberatory furnace and originally was an exact duplication of the fire refining already described. As the cathode copper is already pure, a simple melting is all that should be required, but molten copper is so susceptible to contamination that until recently the gases from combustion, iron in the rabbles, etc., were absorbed to a sufficient extent to require actual refining. At the present time large quantities of cathodes are being added to the molten charge during ladling and earlier, basic furnaces are being substituted for acid ones, thereby suppressing slag formation, and attention is being paid to keeping coal ashes from blowing over from the firebox, so that a true melting without refining is being approached.

It is well known that cathode copper when drawn into wire will show an electrical conductivity some two per cent higher than the same copper after a subsequent fire refining. This is probably due partly to the fact that chemical impurities in the cathode are chiefly present as a mechanical mixture due to adherence of anode slimes which are dissolved in the copper when melted, making a high resistance matrix around the copper crystals when the metal is cast and cooled;

and partly to contamination during melting. It seems probable that the conductivity of perfectly pure soft copper is in the neighborhood of 103 per cent of the Matthiessen standard in common use.

Lake ores are low grade native copper deposits, which are mechanically concentrated to an 85 per cent mineral. This is melted and, after skimming off the slag formed by the remaining gangue, is given a fire refining as previously described. The Michigan mines are among the oldest, largest and deepest in the world. Thirty years ago Lake copper was the standard of the industry. The surface ores were remarkably free from objectionable impurities and copper of the highest conductivity was readily produced. The first electrolytic copper to come on the market was of irregular character due to lack of familiarity with the principles of this new process and for a considerable time Lake copper was deservedly considered superior. With increasing depth, however, many of the mines showed increasing quantities of arsenic and indeed all Lake copper may be considered as arsenical copper, although in some brands the arsenic is very low. The result was that electrolytic copper began to take precedence for electrical work, as its conductivity could be absolutely depended upon, and Lake began to fall back upon superior "working" qualities, a term which defied exact definition.

It is now generally admitted that high conductivity Lake copper cannot be distinguished from electrolytic copper, while low conductivity Lake is really an alloy of copper with arsenic which has certain desirable properties for special uses. Nearly all the elements which markedly depress the conductivity when alloyed with copper are helpful in developing desirable mechanical properties, for example, phosphorus, aluminum and silica. High arsenical copper running about 0.4 per cent arsenic has now a special market for making firebox plates in Germany, and uses are beginning to be found for the intermediate grades. One of the large Lake companies maintains its own electrolytic refinery, and in this way recovers a small amount of silver and eliminates the arsenic, the product still being classed on the market as Lake, although it is equally electrolytic. The old prejudice in favor of Lake on general principles has now largely died out, but only with the contemporaneous retirement of the older generation of wire mill managers. Lake copper should be clearly graded by arsenic contents into a series of alloy coppers, the class at one end competing with electrolytic on its own ground, and the other classes sold in competition with arsenical copper from other sources, a field which has only lately been properly appreciated.

The last class of copper produced which we have to consider is that generally known as casting copper, a very loose term covering a multitude of sins. There are three main sources of casting copper—(a) from converter bar or black copper from smelters whose

ore supply carries quantities of silver and gold insufficient to pay for refining, (b) by-product copper not up to standard electrolytic grade occasionally produced by refineries and (c) the result of smelting scrap reclaimed from all sorts of new and old work. The first is often of excellent quality, one well known brand being maintained at 99.80 per cent Cu or better, and is generally comparable with English Best Selected. The second class is generally an arsenical copper and is not now often seen as the refineries are nowadays able to eliminate arsenic from the process in other ways. The third class is generally foul, but often suitable for common castings as the impurities help the founding, pure copper being a difficult metal to handle in a foundry. The copper contents may run below 99 per cent Cu, however.

Specifications for Lake and electrolytic copper may be readily drawn and after a thorough investigation the American Society for Testing Materials has issued a set which should be generally accepted by engineers, as it has already been by the large refineries and wire mills. Casting copper presents a specification problem hopeless of solution at the present time, as there are well known brands in the market with the widest imaginable range of impurities, all of which are being kept consistently within a certain range of quality for each individual brand and which find a market for various special uses. About the one thing that can be said of casting copper is that neither a conductivity nor a ductility test is applicable in the nature of things.

Turning now to the uses for copper, they may be broadly classified as follows: (a) wire and other shapes for electrical purposes; (b) sheets and plates for non-electrical uses; (c) copper castings, generally for electrical use; (d) in alloys such as brass and bronze; (e) special purposes for which small quantities of alloyed impurities may be advantageous.

Electrical use immediately imposes a conductivity requirement which rules out everything but electrolytic and high conductivity Lake, which, as before stated, are practically identical coppers. Most of the electrolytic refineries figure on averaging about 100.0 per cent soft in the electrical conductivity of their outputs. Occasional lots may reach nearly to 101.0 per cent and some may approach 99.0 per cent, while 98.5 per cent is the usual rejection limit, but it is very unusual for a refinery to ship anything for electrical use which is below 99.0 per cent. No distinction is made between cakes, wire bars and ingots, more than one shape often being cast from a single furnace charge, so that there is nothing to be gained by ordering wire bars and then cutting them up, when ingots are desired. Unless electrical use is specified it is customary to allow an additional leeway of one per cent in conductivity to the refiner, but he rarely needs this and prefers to maintain the higher standard, as copper is often resold several times before it comes into the

hands of the actual user. As copper from a single furnace charge will carry practically uniform chemical impurities, shipments on an individual order should be filled from as few furnace charges as possible and all wire bars and cakes should be stamped with marks identifying these charges. The refiner will always consider complaints on a furnace charge basis if they are of a chemical nature. If they are indefinite he will generally investigate what other customers received copper from the charge complained of, and in the absence of other complaints will demand a bill of particulars before giving the matter serious consideration. The conductivity of a furnace charge is generally determined at the refinery several times while the charge is being cast and this precaution together with the ample margin above rejection limits which is maintained have practically abolished conductivity complaints.

When copper is not to be put to an electrical use conductivity is of no special value except as a certificate of the absence of more than a trace of a certain class of impurities. The refiner divides impurities into three classes; those that depress conductivity, such as arsenic and antimony; those that impair ductility, such as lead, tellurium and bismuth; and those which are of value if reclaimed, such as silver, gold, platinum and palladium. The elements which depress conductivity are kept within bounds by the conductivity test regularly made. Those which are of value if reclaimed will never reach quantities sufficient to affect the physical properties of the copper as it would pay to re-refine any such copper. The remaining class comprising elements which impair ductility is more difficult to deal with.

We know that bismuth, lead, tellurium and probably selenium make copper very brittle even when present in very small quantities. We do not know, however, how to write a specification limiting these impurities as the presence of small amounts of other impurities will neutralize their bad effects. We do know that amounts of lead up to 0.005 per cent have no perceptible effect in mill practice or in alloys. Double this amount shows mild effects. Lead is about the only one of the group ever met with in sufficient quantity to be of interest. As these elements are practically insoluble in copper their effect on the conductivity is directly proportional to the amount present and consequently negligible.

It must be understood that an element like lead is always present in small amounts in refined copper and the mere fact of its presence as shown by a delicate qualitative test is no basis for complaint. It should be further borne in mind that the determination of the small quantities of impurities in refined copper quantitatively can only be done with even reasonable accuracy by a chemist who has had large experience in this particular work. A representative analysis of

refined electrolytic copper would be somewhat as follows:

	Per Cent.
Conductivity (annealed)	100.0
Copper	99.93000
Silver	0.00100
Gold	0.00001
Sulphur	0.00300
Oxygen	0.04000
Iron	0.00350
Nickel	0.00400
Arsenic	0.00200
Antimony	0.00300
Aluminum	0.00100
Phosphorus	Trace
Lead	0.00200
Bismuth	Trace
Selenium	0.00050
Tellurium	0.00050
	99.99051

It will be seen that oxygen is the chief impurity. It has been pretty conclusively shown that too much oxygen makes the copper harder and affects the annealing temperature, the tensile strength of wire and the number of breaks in a wire machine. This may be due to some surface effect as the "set" surface of a wire bar has a greater oxygen content than the body of the bar and as the oxygen content increases it is possible that this oxidized layer becomes thicker. Another point about high oxygen is that it corresponds to low copper contents and to that extent is sold as copper. In brass making the "set" or "pitch" of the ingot is of no consequence except when the most careful work is done when melting in the foundry to avoid further absorption of oxygen. It is obviously useless to impose rigid conditions upon the refiner if the same conditions are not observed in the remelting and it is only at the largest and best equipped brass foundries that such conditions are even approached. When zinc is introduced into molten copper it acts as a deoxidizing agent forming zinc oxide. If the copper is kept at very high pitch this source of zinc loss and dirty brass can be greatly diminished and this fact has resulted in a demand for high copper contents in ingots. It has, therefore, become a general custom to specify that the copper contents of refined copper shall not be less than 99.88 per cent, which really means 99.90 per cent, allowing 0.02 per cent for assay variations. As this is a rejection point the actual average content is expected to be between 99.92 and 99.94 per cent.

When we come to casting copper a far greater leeway must be allowed as already pointed out. In fact, except in considering the price charged for the material, copper contents have but little to do with casting copper. It is best to buy this material on the basis of known brands after finding what brands yield good results in the particular class of work and then insist upon uniform deliveries, judging the material by chemical analysis of the chief impurities.

The physical defects of refined copper are many. Practically all cast copper is porous, doubtless due to the discharge of dissolved gases as the copper cools.

This is analogous to the "piping" of steel ingots, but is not so pronounced because copper is cast in a shallow mold instead of on end. These microscopic bubbles are doubtless the cause of roughness in wire. Then there is a class of defects inseparable from ladling, consisting of cold sets and splashes where the copper has run up on the mold and chilled before the main body of metal reaches that point. Then there is porosity or sponginess of the surface due to the mold being either too hot or too cold. Another defect is raised edges on the set surface, generally due to slightly lowered pitch corresponding to excessive oxygen content of the copper. Should the pitch drop still lower "nigger heads" or little black spots will appear. These are the outlets of gas cavities extending some distance into the copper. On the other hand, should the oxygen content be too low the surface of the bar rises and finally breaks open or "spews," an even worse condition.

Many of these defects are always present in more or less degree. Mechanically ladled copper can never be perfect. Specifications require that copper shall be free from mechanical defects, but a reasonable attitude regarding minor troubles on individual pieces is generally necessary to the peace of mind of a buyer. On the other hand, a refinery occasionally becomes careless in such matters and will send out some surprisingly bad work, so that careful, systematic inspection combined with an attitude of friendly criticism is the best way for a copper producer and a copper user to live together.

U. S. CAN REPLACE IMPORTED ARSENIC.

The consumption of white arsenic in the United States in 1913 amounted to about 7,200 tons, valued at \$570,000, of which 2,513 tons, valued at \$159,236, was produced in this country as a by-product from copper and precious-metal smelters, and the remainder was imported largely from European countries. For the present imports of arsenic will probably be seriously diminished by the European war. The American smelters can save much more arsenic than they do now, for the cheapness of the product has prevented the saving of all that was practicable, and the war would seem to open the way for an increase in the American output. Works for the exclusive production of arsenic have been erected at only two places in the United States—Brinton, Va., and Mineral, Wash. It is difficult for such plants to produce arsenic to be sold in competition with the by-product of the smelters except in periods of high prices, such as may again prevail if the war and its industrial disturbances are long continued.

VANADIUM STEEL RAILS.*

Advance information has been given to *The Iron Age* of an extended series of tests of vanadium steel rails compared with tests of carbon steel rails of like section and manufacture. The tests cover the investigation of several heats of basic openhearth vanadium steel rolled into rails by the Cambria Steel Company for the American Vanadium Company, Pittsburgh, from which company undoubtedly the full report may be soon obtainable. An important conclusion from the test is the recommendation by the American Vanadium Company of following chemical specifications for vanadium steel rails:

Carbon	0.45 to 0.60 per cent
Manganese	1.00 to 1.25 per cent
Silicon	over 0.10 per cent
Phosphorus	not over 0.05 per cent
Sulphur	not over 0.05 per cent
Vanadium	4 lb. added per gross ton

This specification, it is explained, will give rails with 30 to 50 per cent higher elastic limits or useful strength, combined with greater toughness and hardness than simple carbon steel rails with 0.62 to 0.75 per cent carbon content. It is explained further that the vanadium steel rails show greater superiority in comparison with carbon steel rails of 0.45 to 0.60 per cent carbon. It is believed that the relatively low percentage of carbon recommended, together with the freedom from segregation of vanadium steel, should result in the practical elimination of the danger of failure from internal fissures.

The tests cover drop tests, tensile tests, alternating impact tests, bend tests, hardness tests and wear tests. In the manufacture of the rails, it was found that no change was required from that followed in the usual practice. There was no tendency for cracking or tearing and in rolling the vanadium steel took the same standard gauges as the simple carbon steel. The chemical composition of the three heats from which the rails were rolled and the production figures are given in the following table:

Heat number	26,813	27,989	27,993
Carbon, per cent.....	0.55	0.51	0.558
Manganese, per cent...	1.51	1.11	0.78
Silicon, per cent.....	0.17	0.12	0.158
Phosphorus, per cent..	0.015	0.010	0.017
Sulphur, per cent.....	0.019	0.029	0.025
Vanadium, per cent....	0.148	0.146	0.156
Actual per cent vanadium added	0.168	0.16	0.177
Ingots, weight, lb....	121,000	104,400	108,000
Rails, weight, lb.....	89,500	79,900	82,000
Rails, number.....	{ 77—1st & 5—2nd	{ 73—1st & 1—2nd	{ 73—1st & 2—2nd
Rails—scrap.....	none	none	none
Yield, per cent.....	74.0	76.9	75.9

The usual requirement for drop tests was followed, except that the height of the drop was increased from 15 ft. to 18 ft. for the vanadium steel rails, but two rails from the first heat were tested with the height of drop of 15 ft. to get a direct comparison with carbon

steel rails. To determine the ductility or stretch after each blow of the drop, six 1-in. spaces were laid off on the bottom of the flange. The tables of the report give in detail the number of drops which each specimen withstood and in detail the elongation of each of the six divisions. The vanadium rails showed up stiffer under the drop test of carbon steel rails, which were of 0.62 to 0.75 carbon specification; 0.60 to 0.90 per cent manganese; silicon under 0.20 per cent and phosphorus under 0.04 per cent.

The tensile test showed an increase in elastic limits or useful strength in favor of the lower carbon vanadium steel without sacrifice of ductility. The bend tests were made on rectangular pieces about 8 in. long. The load was applied 6 in. from the fixed end of the test piece. The radius of the jaw holding the bent specimen was not over $\frac{1}{8}$ in. and the edges of the specimen were not rounded. The alternating impact tests were made on bars turned to $\frac{3}{8}$ in. diameter, and in connection with these tests are given sections of rails to indicate the portions of the rail from which test pieces were taken, so that the conditions of various parts of the rail could be studied. In the impact test the bar was held firmly in a vise and the upper end moved backward and forward by means of a slotted arm to a total distance of $\frac{3}{4}$ in. at the rate of 600 movements per minute. The hardness tests were made by the Brinell method, and readings were taken for 35 different points in the cross section of each rail. The sections from heat 26,813 showed an average hardness of about 340; heat 27,989, about 302; heat 27,993, about 293; the carbon rail A about 248 and carbon rail B about 269. The tests indicated that the vanadium steel rails, although lower in carbon, have greater hardness and hence correspondingly increased resistance to wear.

For securing a wear test, imitating the action of a car wheel on the rail, a piece 1 in. long and 1 in. in diameter was rotated between three manganese steel rollers, 3 in. in diameter. The two bottom rollers were driven by gears with a different number of teeth, to give the rollers different speeds and cause the test piece to slip, as well as to rotate. A load of 110 lbs. was applied to the test piece by loading the top roller. In previous tests a load of 220 lbs. was applied. Owing to a tendency found with rails like carbon rail A to flow and form a fin or bead, which gave trouble, the weight was reduced to 110 lbs. It was found that the abrasion of the test piece was better with this weight than with the heavier load. The test pieces were weighed before and after the test and the loss of weight in milligrams was divided by the original weight to obtain comparative figures. All tests were run for 50,000 revolutions. The relative wear of the vanadium steel rail was found to be practically one-half that of the carbon rails.

*From *The Iron Age*.

MANGANESE BRONZE AS ENGINEERING MATERIAL.*

By LOUIS P. WEBBERT.†

The use of manganese bronze as an engineering material covers a period of about twenty-five years. In fact the development of this alloy has been due primarily to the discovery of P. M. Parsons of London, England, who ascertained that when a small quantity of aluminum is added to melted brass high in zinc, a remarkably fluid metal is produced. This discovery enabled him to produce sound and clean castings.

Manganese bronze has an established place among engineering materials today on account of its great strength, non-corrodibility, moderate cost, wide scope of application and simple method of manufacture. It receives its name from the metal manganese which is a constituent part of the alloy. However, the term bronze is correctly applied only to those alloys composed of tin and copper and there was a time when the term bronze was applied to any new alloy for which its discoverer fancied great possibilities. The alloy manganese bronze therefore is incorrectly named. Technically speaking, it is a brass containing small amounts of tin, iron, manganese and aluminum.

COPPER-ZINC ALLOYS.

If manganese bronze is a brass, strictly speaking, how is it related to other alloys of copper and zinc? Why does this alloy possess more strength than other alloys of copper and zinc, and why can its physical properties be easily affected by slight changes in chemical composition? The curves in Fig. 1 will assist in showing the variation in the strength and properties of copper-zinc alloys and will enable us to understand why manganese bronze contains the proportions of copper and zinc which are prescribed for it. By means of these curves Charpy (Bulletin de la Société des Alliages) shows the variation in the strength and ductility of cast copper-zinc alloys containing different percentages of copper and zinc. The curves begin showing the tensile strength and ductility of pure copper. Then with increasing percentages of zinc and decreasing percentages of copper, as shown at the top and bottom of the curves, the tensile strength increases gradually at first, then rapidly up to a composition of about 56 per cent copper and 44 per cent zinc. After this point is passed there is a decided drop in the tensile strength when the alloys become brittle with increase in zinc. Beyond 50 per cent zinc the tensile strength curve is of no interest. The ductility or percentage elongation curve reaches a maximum before the tensile strength curve reaches its maximum.

The fluidity of the melted metal varies with the increase in zinc. Although this property cannot be

measured it is known that the alloys of copper and zinc showing the highest tensile values on the curve are sluggish metals in the fluid state and when cast give bad and dirty castings. P. M. Parsons, who began the development of manganese bronze in 1876 by introducing iron and manganese into his brass mixtures, met with this trouble. He discovered that in adding a small quantity of aluminum to his melted alloy, the metal became very fluid and as a result he obtained clean and sound castings. He procured a patent for his new alloy in 1888.

If, given the curve in Fig. 1, we should be asked to produce a copper-zinc alloy giving the highest tensile strength, we would choose an alloy at the peak of

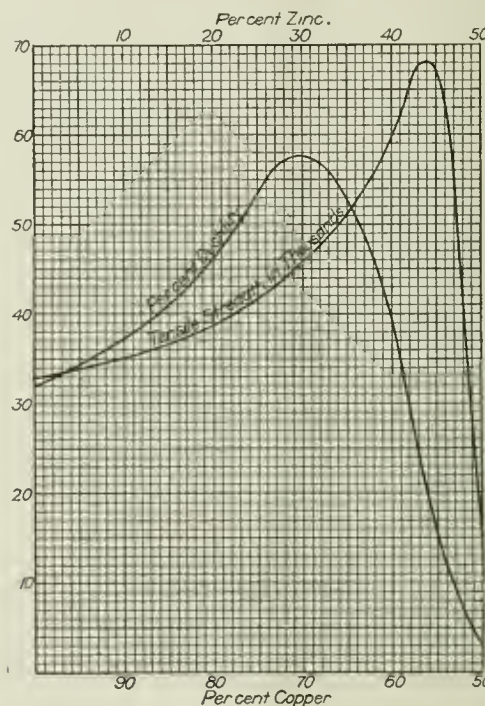


Fig. 1.—Charpy Curves Showing Strength and Ductility of Copper-Zinc Alloys.

the curve giving 56 per cent copper and 44 per cent zinc. The elongation at this point is about 20 per cent. After having studied the effects of tin, iron, manganese and aluminum upon copper-zinc alloys, we should add sufficient amounts of these metals; we would then have our present formula for manganese bronze.

The specifications given in Table I show the chemical and physical requirements.

EFFECT OF METALS ON MANGANESE BRONZE.

In these specifications it will be noted that small additions of tin, iron, aluminum and manganese are required to give the best results. The effects of the different metals are described in the following paragraph:

Tin.—Tin is added to manganese bronze to give added strength and an increase in the yield point. With increasing amounts of tin the ultimate tensile strength and yield point are increased until a percentage of about 0.8 is reached. Beyond 0.8 per cent there is a further increase in the ultimate tensile

*From The Iron Age.

†Chemical engineer, Bath Iron Works, Bath, Maine.

strength and yield point of the alloy but a marked effect is produced on the ductility which is lowered. This indicates that increasing the tin beyond 0.8 per cent tends to make the alloy brittle. The amount usually added is 0.75 per cent.

Iron.—Iron increases the strength of manganese bronze and raises the yield point. The importance of having this metal present lies in the property that iron has of closing the grain of the alloy. Without iron the grain of manganese bronze would not be small but would show up coarse in the fracture. A fine grain is desired because the finer the grain or structure the stronger the metal. In forging a bar of manganese bronze or steel the granular structure is broken up and made smaller to produce a stronger metal. The amount of iron usually added in making manganese bronze is about 0.7 per cent although this is sometimes run up as high as 1.50. Marine engineers object to the presence of more than one per cent of iron in the alloy and claim that the presence of more than one per cent causes corrosion in sea water.

in the presence of aluminum. In the manufacture of manganese bronze the best metals are selected because these metals are most free from lead. The maximum amount of lead permissible in manganese bronze is 0.2 per cent. The less there is present the better.

Copper.—In the alloying and remelting of manganese bronze a certain amount of zinc is lost from the crucible through volatilization, the loss being about three-fourths per cent in each melting. This loss causes a decrease in the zinc with a corresponding increase of the amount of copper in the alloy. If the greatest strength is desired an increase in the percentage of copper is to be avoided, which is easily understood by referring again to the curve in Fig. 1. With the aid of chemical analysis the loss of zinc is determined for each heat and an amount of zinc equal to the loss of zinc is added to the crucible in the remelting of the metal before the bronze is poured. Due to this loss of zinc it is necessary to have the manufacture of manganese bronze under chemical control in order not only to obtain the strongest castings but to keep the composition uniform.

TABLE I.—SPECIFICATIONS FOR MANGANESE BRONZE.

	Copper, per cent.	Zinc, per cent.	Tin, maximum per cent.	Iron, maximum per cent.	Aluminum, maximum per cent.	Manganese, maximum per cent.	Lead, maximum per cent.	Tensile strength, lbs. per sq. in., minimum.	Yield point, lbs. per sq. in., minimum.	Elongation, in in., per cent.
American Society for Testing Materials	55 to 60	39 to 45	2.00	2.00	0.50	0.50	...	70,000	...	20.0
Bureau of Steam Engineering, U. S. }	57 to 60	37 to 40	0.75*	1.00	0.50	0.30*	...	60,000	30,000	20.0
Navy	56 to 58	40 to 42	1.00	1.00	0.50	0.30	0.20	65,000	30,000	20.0

*Percentages desired.

Aluminum.—Aluminum, as previously mentioned, is added to obtain fluidity of the metal in pouring. From 0.3 per cent to 0.5 per cent is a sufficient quantity to have present. An increase of the amount of aluminum does not give an increase in the strength. Some metallurgists claim that a larger amount of aluminum added than is necessary to obtain fluidity is undesirable because this metal oxidizes readily. The oxides become included in the metal producing a weaker alloy.

Manganese.—Manganese is added as a deoxidizing agent; 0.3 per cent is a sufficient quantity to have present in the alloy. When the amount is increased manganese adds hardness and strength but not to such a marked degree as iron. Some metallurgists employ a high percentage of manganese to impart strength to their bronze, using as high as three per cent manganese. The writer uses iron to obtain strength and manganese as a deoxidizer. The amount of manganese in the alloy does not stay constant but "burns out" of the metal in two or three successive meltings.

Lead.—Lead is a metal whose presence is not desired in bronze. Lead weakens the alloy especially

Table II gives the chemical analyses and physical tests of some castings, some of which were satisfactory, and others not. These results are given to show the effect chemical composition has upon the physical properties of manganese bronze. Numbers 1, 2, 3 and 4 are satisfactory both chemically and physically. Numbers 4 and 5 differ in the percentage of iron, otherwise they are quite similar in chemical composition. In numbers 6 and 7 the tin is too low. Alloys 8 and 9 contain too much copper and very little iron. In number 9, however, the high tin counteracts the effect of high copper and low iron.

MANUFACTURE OF MANGANESE BRONZE.

As stated in a previous paragraph, only the best metals obtainable are used for making manganese bronze on account of the very small amount of lead present in the metals. The copper is melted first under charcoal. An alloy composed of iron, manganese and tin is placed on top of the charcoal and when heated to redness is pushed into the melted copper. The proper amount of aluminum is next added. The metal is well stirred. The union of the aluminum with the copper causes an increase in the temperature of the mixture at which temperature all of the iron-man-

ganese-tin alloy should dissolve. The zinc is next added to complete the mixture. The iron-manganese-tin alloy, commonly called "steel alloy," is made by melting together wrought iron, and ferro-manganese. When melted the tin is added to lower the melting point of the alloy. The proportions used are the following: Wrought iron, 18 lbs.; ferro-manganese, 4 lbs.; tin, 10 lbs. These proportions can be varied, of course, to obtain a convenient alloy for any composition of manganese bronze. Using the steel alloy is the most popular method for introducing iron into the molten metal.

Another method for introducing the iron consists in plunging thin iron plates into the melted copper and causing the iron and copper to unite directly. The difficulty experienced in using this method lies in keeping the surface of the iron plates clean or free from oxide. Iron and copper unite readily when both reach the same temperature in the crucible at about 2300 deg. F. provided the surface of the iron is per-

are added after the aluminum-zinc. After the last piece of zinc has alloyed with the metal, the whole heat is thoroughly stirred, the crucible is removed and the metal pigged. The alloy of manganese-copper, obtainable on the market, can be had as the following compositions:

Manganese-copper: Manganese, 28 to 30 per cent; iron, 2 to 3 per cent; remainder, copper.

Manganese-copper, carbon free: Manganese, 30 per cent; copper, 70 per cent.

Manganese-ferro-copper, carbon free: Manganese, 30 per cent; iron, 20 per cent; copper, 50 per cent.

Manganese bronze is always remelted to obtain a homogeneous alloy and to free any included oxide in the metal. The first mixing is done in the crucible by means of the stirrer; the second when the metal is poured into the chills; and the third mixing is done when the pigs are remelted in the crucible. After the last pig of metal has melted the temperature of the metal is allowed to rise to the proper casting temperature (1800 to 1900 deg. F.), then removed from the furnace to the mold and cast.

TABLE II.—CHEMICAL ANALYSES AND PHYSICAL TESTS OF MANGANESE BRONZE CASTINGS.

Test No.	Copper, per cent.	Zinc, per cent.	Tin, per cent.	Aluminum, per cent.	Iron, per cent.	Manganese, per cent.	Lead, per cent.	Tensile strength, lbs. per sq. in.	Yield point, lbs. per sq. in.	Elongation, per
1	57.66	39.85	0.84	0.58	0.69	0.15	Trace	73,885	...	26
2	57.14	40.49	0.76	0.46	0.92	0.13	0.20	70,850	...	32
3	56.09	41.63	0.80	0.44	0.70	0.32	Trace	79,500	...	24
4	55.85	41.88	1.06	0.17	0.69	0.37		73,460	35,000	22
5	56.38	42.22	1.01	0.08	0.23	0.08		71,060	34,000	18½
6	56.86	40.17	0.41	0.55	0.26	0.08	0.20	65,300	31,000	26
7	57.52	40.96	0.30	0.48	0.56	0.11	0.07	67,300	27,500	34
8	58.00	40.70	0.78	0.32	Trace	0.30	0.00	65,650	28,800	29
9	58.02	40.17	1.29	0.15	0.18	0.15	0.04	69,100	32,500	25

fectly clean. If not, the iron is left undissolved and when it reaches the surface of the metal there is further oxidation of the iron which renders combination with the copper impossible. No difficulty is experienced in the use of this method when galvanized sheet iron of about 0.03 in. in thickness is used. Galvanized sheet iron is made of the best open-hearth iron and furnishes a splendid form of iron. Strips of the sheet iron about 2½ ins. wide are bent into the form of a spiral and plunged into the melted copper. The covering of zinc is immediately dissolved off the iron allowing a clean surface to be exposed to the copper. The iron is not allowed to become exposed above the surface of the copper. When the temperature of the copper reaches approximately 2300 deg. F. solution of the iron takes place. The manganese is added before the iron is introduced in the form of manganese-copper (carbon free). This alloy is placed on top of the charcoal and when red hot is pushed into the copper. The aluminum is added after the iron preferably in the form of aluminum-zinc in which form it combines more quietly with the metal in the crucible than when used in the form of the metal itself. The tin and zinc

MANGANESE BRONZE FROM OTHER ALLOYS.

In large manufacturing plants high grade brass stock material is cut up for manufacture into many products. In the process of manufacturing these products waste material is always produced. Ordinarily this waste material (tubing, sheet brass, etc.) is turned over to the foundry as scrap brass to be used for brass castings. When a laboratory is connected with the plant a greater value can be placed upon this scrap material since it can be made into manganese bronze. This waste material was originally made of the best metals obtainable and is composed of copper and zinc with an occasional small amount of tin present. When this material arrives at the brass foundry it is melted and cast into pigs. Brass turnings are treated in a similar manner. A chemical analysis is made of each heat. The metal of those heats that contains more than 0.20 per cent of lead is allowed to go into the manufacture of brass castings. Those heats that contain less than 0.20 per cent of lead are reserved for the manufacture of manganese bronze. When using brass for bronze a bath of melted copper is first made to dissolve the "steel

alloy" or iron and manganese-copper, then the brass pigs are added and lastly the proper amount of aluminum or aluminum-zinc, tin and zinc necessary to give the correct composition to the alloy. Sometimes the brass contains sufficient tin to give the desired percentage of tin to the manganese bronze after the mixture has been made; sometimes it contains more and sometimes less. All calculations are based upon the chemical analyses of the brass heats. In Table 2, tests 1 and 2 were made on manganese bronze made from scrap brass. The results obtained show satisfactory metal.

MANGANESE BRONZE CASTINGS.

When changing from a fluid to a solid state manganese bronze, like all strong metals, shrinks in the mold. On account of this shrinkage skillful molding is essential to obtain sound castings. The molding methods will not be discussed in detail. It will be sufficient to state that risers are placed on heavy parts of a casting to furnish metal to the casting when the metal shrinks. Where no risers can be used chills are placed at the thickest parts of the casting. Fig. 2 shows three types of manganese bronze castings. The one to the left is a gear blank with the gate cut off and is representative of a class of heavy castings made of this metal. The other two show castings that are typical of a class where lightness and great strength are required. In the central one the ribs and flanges are $\frac{1}{8}$ in. in thickness, and risers are shown at the heaviest parts of the casting. The other light casting is a hoisting drum for a large racing yacht. The dimensions are: Length, 36 ins.; diameter of drum, 18 ins.; thickness of top and bottom rims, $\frac{3}{16}$ in.; thickness of drum, $\frac{3}{8}$ in. Chills were used at the thickest parts of this casting.

CONCLUSIONS.

Considering the scope of application of manganese bronze it is easy to conclude that it can compete with other non-ferrous metals where strength and cost are important considerations. It can also compete where strength and lightness are important factors due to its great tensile strength and the thin sections into which it can be cast.

It has been shown that there can be practically but one composition for the copper-zinc alloy if an alloy of the greatest tensile strength is desired and that additions of small amounts of other metals improve the casting qualities and increase the strength. Manganese bronze can be correctly named a brass. Where scrap brass is of such quality that it can be converted into manganese bronze, such scrap becomes a valuable source of profit.

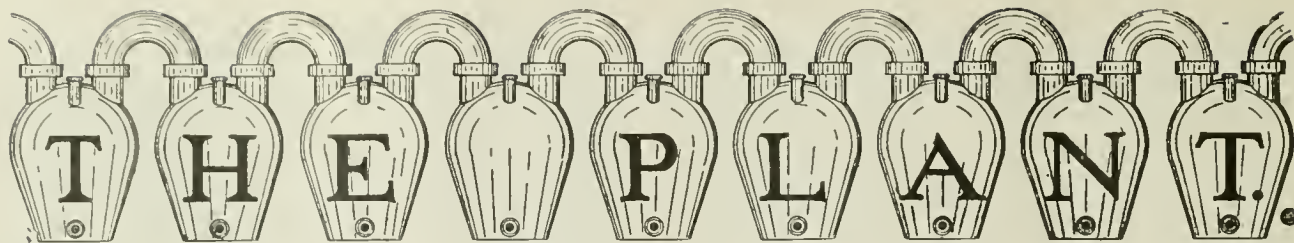
ARKANSAS LARGEST PRODUCER OF ALUMINUM ORE.

Arkansas is first among the states in the production of two minerals—bauxite and novaculite, the former being the ore of aluminum and the latter the source of the larger part of the oilstones produced in the United States. The principal mineral product of Arkansas, however, is coal, the annual value of which constituted over 50 per cent of the State's total. The total value of all the mineral products of Arkansas in 1913 was \$6,780,760, according to the United States Geological Survey, compared with \$6,258,726 in 1912. The coal production was 2,234,107 short tons, valued at \$3,923,701 in 1913, against 2,100,819 tons, valued at \$3,582,789, in 1912. The coals of Arkansas are generally of high grade, particularly in the eastern part of the coal field, where they approach anthracite in character. The semianthracite of Arkansas is an excellent domestic fuel and reaches markets as far north as Kansas City. Bauxite, from which aluminum is derived, is second among the mineral products of the state. It is mined near Benton, in Saline county, and in Pulaski county. In 1913 the stone quarries of Arkansas furnished products valued at \$525,050, exclusive of novaculite and of limestone burned for lime. In 1912 the quarry products were valued at \$513,844. The clay-working industries, while not highly developed, take third place and in 1913 produced an output valued at \$529,624, an increase of \$67,019 over 1912. The sand and gravel pits yielded \$320,639 in 1913 and \$393,639 in 1912. The only metalliferous products of Arkansas besides bauxite are lead, zinc, and manganese ores. Other commercial mineral products are fuller's earth, gems and precious stones, lime, mineral waters, natural gas, phosphate rock, and slate.

The Standard Oil Co. of New Jersey has just completed a new refinery at Tampico, construction having required about 18 months. It is a 4-still refinery, built especially to refine Mexican crude oil, and has a daily capacity of 4,000 bbls. of distillate. At present it will be used only as a topping plant, and the topped oil (distillate) will be shipped to the United States for further refining. The plant is on a 754-acre tract along the Panuco River, facing the Gulf of Mexico. A 400-ft. pier extends into the river, where a 30-ft. channel has been dredged. A pipe line has been laid from the Huasteca Petroleum Co.'s tank farm to the Standard property, and all the oil contracted for by the Standard will be pumped direct to the new refinery, where it will be topped and placed on storage in 55,000-bbl. tanks. The pumping station has a capacity of loading 50,000 bbls. on board steamers in 12 hours.

Primary lead production in 1913 in the United States for domestic ores was 436,430 short tons, valued at \$38,405,840.

The cotton export trade of Germany, although confined to neighboring European countries, amounted to 108,093,951 lbs. in 1912 and 106,460,544 lbs. in 1913.



REFINING PETROLEUM BY LIQUEFIED SULPHUR DIOXIDE.*

By DR. L. EDELEANU.

Crude petroleum is a mixture of various groups of hydrocarbons and some bodies containing oxygen or sulphur. These constituents possess properties differing considerably one from another and the proportion in which they are contained in the crude oils is also very different.

Owing to this complicated composition the practical use of crude petroleum is much restricted.

For example it is sometimes used as a liquid fuel. But its employment in this way is uneconomical because various valuable qualities of the individual constituents are not made use of.

The rational utilization of petroleum can only be accomplished if the various groups of hydrocarbons are separated. The mixture of hydrocarbons present in the crude oil must be split up in such a way that the hydrocarbons are divided into various groups having predominant characteristics and uses. To accomplish such a separation is the aim of the technical refining of petroleum.

ORDINARY REFINING BY DISTILLATION AND CHEMICAL TREATMENT.

Hitherto this has been accomplished by two processes, namely, fractional distillation and chemical treatment of the distillates obtained.

Distillation Process.—The process of distillation consists in the separation of the constituents of petroleum into various fractions, the boiling points of which lie within certain defined limits. The fractions so separated possess certain special qualities in common, which enable them to be applied for specific purposes in practice. For example, we have the fractions known as benzene, illuminating oils, heavy oils, lubricating oils, etc.

The benzene fraction, which contains the readily volatile hydrocarbons, furnishes chiefly the well known solvents, and is now mainly used for producing the driving power for automobiles.

The intermediate fractions boiling up to about 300° C. are the oils used for purposes of illumination. This product must comply with several requirements. It should not smoke, should not possess any unpleasant odor, and should give a bright and steady flame which does not undergo unduly great alterations while burning. Now these conditions are only complied with by

using oils of certain origin, while many of them do not fulfill the requirements in the least; it is therefore one of the special problems in refining to convert these inferior varieties into good burning oils.

The heavier fractions are used as gas oil or material for Diesel motors and the more viscous fractions are employed as lubricants.

For the use of lubricants these fractions must possess a viscosity which should be retained to certain limits of temperature variation, such as are commonly met with in the practical use. Moreover, there must be no deposit of free carbon and they must be freed from components which at high temperature would form a deposit of char and thus diminish the value of the lubrication.

Now the object of the petroleum refinery cannot be achieved by distillation alone. In fractional distillation it is inevitable that some varieties of hydrocarbons having the same boiling point will find their way into certain fractions, notwithstanding the fact that their chemical properties are distinctly dissimilar. Distillation alone is thus quite unsuitable. The problem to be solved is how to obtain only the valuable hydrocarbons, and to eliminate those with undesirable or injurious properties.

Refining with Sulphuric Acid.—Consequently recourse has been had to the chemical treatment of petroleum. In this treatment sulphuric acid is mainly used for the purpose of removing the resinous matters and certain hydrocarbons such as olefines. These constituents are separated out in the form of residual sludge—impurities which can be utilized in practice only with extreme difficulty or possibly not at all. For the removing of the aromatic hydrocarbons considerable quantities of sulphuric acid sometimes in the state of "fuming acid" have to be used according to the proportion of these hydrocarbons present in the distillate and this renders the process distinctly costly. The application of large quantities of sulphuric acid and especially in the state of fuming has a further drawback. It does not attack only the aromatic and unsaturated hydrocarbons, but also destroys a certain quantity of the saturated constituents. The process has thus the disadvantage of still further reducing the proportion of useful hydrocarbons finally obtained.

In order to avoid the drawbacks of the treatment hitherto employed, it is necessary to abstain from the purely chemical treatment and to substitute a physical method of extraction. The constituents of the petroleum must be treated with a solvent which dissolves the hydrocarbons of the unsaturated aromatic group

*From Transactions of American Institute of Mining Engineers; paper presented at Pittsburgh meeting, October, 1914.

but leaves the saturated hydrocarbons undissolved. In this way the two classes of hydrocarbons can be separated from one another and employed in the way for which they are suited.

The most important point in the solution of this problem consisted in the discovery of an appropriate solvent and finally liquefied sulphur dioxide was found to be the best material. This substance readily dissolves the unsaturated hydrocarbons, which are responsible for the unsatisfactory burning and odor characteristic of certain illuminating oils, and leaves undissolved the useful illuminating oil. Frasch attempted to achieve the same object by the application of alcohol, but liquefied sulphur dioxide has certain advantages which alcohol has not. The chief advantage, apart from cheapness, consists in the fact that liquefied sulphur dioxide can be readily recovered from the solution, so that in practice the solvent can be used again and again in a cycle of operations, without any appreciable loss.

NEW REFINING PROCESS WITH LIQUEFIED SULPHUR DIOXIDE.

The new process makes use of this peculiar property of liquid sulphur dioxide. If the distillate is agitated with liquid sulphur dioxide at a low temperature the aromatic compounds are dissolved, but the paraffins and naphthalenes are unaffected. Moreover, owing to the difference in the specific gravity, two distinct layers are formed so that it is quite easy to separate them from one another.

The process is comparatively simple. A certain quantity of the sulphur dioxide is added to the petroleum distillate and is dissolved. This addition is continued until the distillate is saturated, and, from that point, each added portion of sulphur dioxide dissolves the aromatic constituents and separates out with them as a distinct layer. Thus, as the treatment is continued, the distillate becomes poorer and poorer in aromatic hydrocarbons until ultimately a refined distillate is obtained, which contains only a small amount of sulphur dioxide, and is practically free from the objectionable aromatic constituents.

It may be observed that the nature of this operation depends to some extent on the temperature. With a rising temperature the solubility of the paraffin hydrocarbons and the naphthalenes—which at low temperatures are practically insoluble—increases rapidly; whereas the aromatic hydrocarbons are soluble in sulphur dioxide at *all* temperatures. It is therefore important that the temperature should be maintained at a suitably low level, particularly in the case of distillate rich in aromatic hydrocarbons. The degree to which the process is affected by the temperature naturally depends on the nature of the material treated. For instance, in the case of a distillate from Borneo, which contained as much as 40 per cent of aromatic hydrocarbons, treatment with 66 per cent liquid sulphur dioxide at -7° C. produced no separation; but a consid-

erable proportion of the aromatic constituents could be separated at -10° . On the other hand, in the case of a Mexican distillate, which only contained about 17 per cent of aromatic hydrocarbons, treatment with an equal amount of liquid sulphur dioxide produced separation even at a temperature higher than $+10^{\circ}$ C. In practice it is found that each distillate requires special treatment, according to its composition, in order to obtain the best result.

This process, which is now being used on a large scale in the petroleum industry, has been worked out by the author also as a laboratory method. For the experiments he uses:

1. A strong-walled graduated burette of 200 cm. contents drawn out pear-shape like on each end with

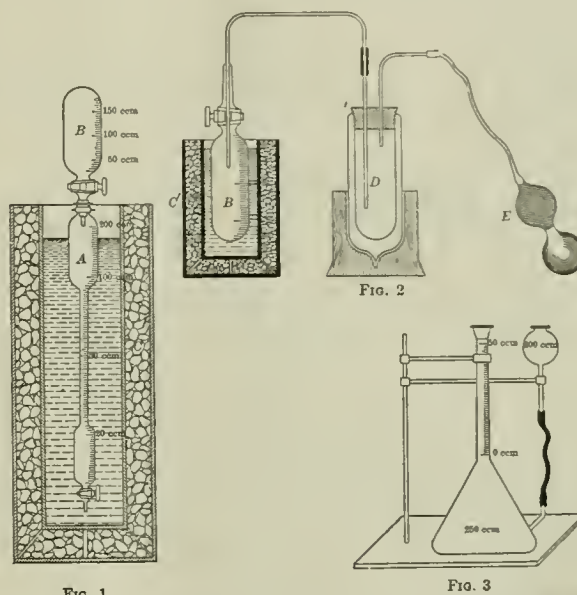


FIG. 1

FIG. 3

a delivery cock protected against being forced out. (See Fig. 1, A.)

2. A strong-walled cylindrical graduated vessel of about 230 cm. contents with a delivery cock also protected against being forced out. (See Fig. 1, B.)

3. Two cooling baths for vessels 1 and 2. The cooling bath is insulated on the outside by means of cork sheets and consists of two tin cylinders which telescope into each other concentrically. The outer cylinder contains a freezing mixture, and the inner a liquid which conducts cold, preferably a distillate of illuminating oil. (See Figs 1 and 2, C and C'.)

4. A flask with a graduated neck and a funnel attached to it. (See Fig. 3.)

5. A sprinkling flask for liquefied sulphur dioxide, consisting of an evacuated double-walled Dewar vessel. (See Fig. 2, D and E.)

To carry out the experiment, one proceeds as follows:

The graduated burette is filled with 50 cm. of the distillate to be examined, and the cylindrical vessel with double the quantity of the distillate of liquefied

sulphur dioxide. Both liquids are cooled in the cooling bath to -12° C. The filling of the cylindrical vessel with sulphur dioxide is demonstrated on Fig. 2. Then the cylindrical vessel is connected, by means of a tight-closing cork stopper, with the burette, and the connection is reinforced either by copper wire or by a suitable clamp. Then sulphur dioxide is allowed to flow from the cylindrical vessel into the burette until in the lower part of the burette, after shaking, a permanently remaining layer is observed. Then one-third the quantity of the balance of sulphur dioxide is allowed to run into the burette. It is again cooled to -12° C., shaken, and then the lower layer is drawn

off into a Dewar vessel. In the same manner, the remaining portion of the sulphur dioxide is introduced, and the sulphur dioxide solution is subsequently allowed to run into the same vessel. Finally, the non-dissolved saturated hydrocarbons remain in the burette.

In treating high-boiling distillates, such as gas oil or lubricating oil, it is sufficient to allow the sulphur dioxide to escape from the two separated products and to establish the ratio of the two groups of hydrocarbons, either by direct weighing or by specific gravity.

In treating relatively low-boiling distillates, such as benzine and illuminating oil, losses may be suffered if the sulphur dioxide is allowed to evaporate voluntarily. In order to avoid these losses it is preferable not to evaporate the sulphurous acid, but to absorb it in a closed vessel by means of an alkaline solution. In this case, one proceeds as follows:

After the sulphur dioxide solution has been drawn off, the burette is connected, by means of a cork stopper, with a glass vessel, and gradually under stirring the oil layer treated with sulphurous acid is allowed to run into an alkaline solution. After all the sulphurous acid has been neutralized and the contents of the vessel has been cooled, the stopper is opened and water is allowed to run in until the whole quantity of the oil has cooled in the graduated part of the neck. Then the volume of the oil layer is determined; also the specific gravity, and from the obtained data the quantity of the saturated hydrocarbon is established. The difference between this weight and the weight of the original distillate gives the difference of aromatic and cyclic unsaturated hydrocarbons.

Table I gives the results of a very large number of experiments with illuminating oil of various origin. Further experiments to extend this method also for the examination of crude oil are in the course of being worked out.

The removal of the aromatic hydrocarbons from an illuminating-oil distillate causes not only a lowering of the specific gravity, but also the raising of the burning capacity and illuminating power. The richer a distillate is in aromatic and heavy hydrocarbons, the more distinctly stands out the improvement brought about by treatment with sulphurous acid. The effect of the new process is clearly discerned when treating a Bustenari distillate. Whereas the chemical process hitherto employed produces a very inferior illuminating oil which smokes badly, and when burned in a 14-unit Cosmos burner develops only 7 cp., the treatment with liquid sulphur dioxide produces an oil equal in quality to the best American and Russian oils.

Table II illustrates the action of the old and new methods respectively on distillates of various origin. See also the graphical comparison in Fig. 4.

TABLE I.—EXPERIMENTS WITH ILLUMINATING OIL DISTILLATES.

Origin of Petroleum.	A.	B.	C.	D.
Europe—				
<i>Roumania:</i>				
Bustenari	0.8195	0.8030	75.0	25.0
Cămpina	0.8125	0.7968	82.9	17.1
Moreni	0.8185	0.8050	77.0	23.0
Timba	0.8195	0.8090	82.5	17.5
Filipești	0.8104	0.7984	84.7	15.3
Policiori	0.8073	0.7955	84.3	15.7
<i>Galicia:</i>				
Urycz	0.8230	0.8105	80.6	19.4
Rogi	0.8120	0.8010	81.3	18.7
Tustanovice	0.8105	0.8000	80.8	19.2
Boryslaw	0.8166	0.8028	83.1	16.9
<i>Germany:</i>				
Wietze	0.8200	0.8098	87.4	12.6
Pechelbronn	0.8058	0.7992	92.3	7.7
<i>Scotland</i>				
	0.800	0.7815	78.3	21.7
	0.7915	0.7807	80.4	19.6
<i>Italy</i>				
	0.8030	0.7902	64.7	35.3
Asia—				
<i>Russia:</i>				
Bibi-Eybat (Baku)	0.8160	0.8085	92.7	7.3
Bibi-Eybat (Baku)	0.8145	0.8092	91.7	8.3
Balachany (Baku)	0.8192	0.8150	93.1	6.9
Grossny	0.8170	0.8072	85.6	14.4
Grossny	0.8155	0.8062	83.4	16.6
Maikopp	0.8165	0.800	71.5	28.5
<i>British-India:</i>				
Burmah	0.814	0.799	80.7	19.3
Burmah	0.817	0.800	80.1	19.9
Burmah	0.840	0.8265	83.2	16.8
<i>Persia</i>				
	0.7988	0.7862	83.2	16.8
<i>Holl. India:</i>				
Borneo	0.8480	0.8035	58.6	41.4
Borneo	0.8505	0.8090	55.5	44.5
Sumatra	0.7994	0.7865	83.8	16.2
America—				
<i>United States:</i>				
Pennsylvania	0.7960	0.7920	93.5	6.5
Ohio	0.7990	0.7926	95.1	4.9
Ohio	0.7985	0.7892	90.9	9.1
Texas	0.8240	0.816	87.5	12.5
California	0.8098	0.7982	85.0	15.0
California	0.8100	0.803	90.5	9.5
California	0.8124	0.8015	81.8	18.2
California	0.8190	0.8112	80.8	19.2
California	0.8195	0.8084	81.4	18.6
California	0.8194	0.8112	85.6	14.4
Mexico	0.8020	0.7926	84.0	16.0
Mexico	0.8030	0.7930	83.9	16.1
Mexico	0.8022	0.7972	82.9	13.1
<i>Peru:</i>				
Lobitos	0.8174	0.807	81.8	18.2
Lobitos	0.8175	0.8122	89.5	10.5
Argentina	0.800	0.793	90.7	9.3
Argentina	0.810	0.804	90.4	9.6
Africa—				
Egypt	0.8104	0.7976	82.5	17.5

A = Specific gravity before treatment with SO_2 ; B = specific gravity after treatment with SO_2 ; C = paraffin and naphthene-hydrocarbons in per cent by weight; D = aromatic and cyclic unsaturated hydrocarbons in per cent by weight.

Utilization of By-Products—The extract obtained in addition to illuminating oil contains, as mentioned, aromatic hydrocarbons and hydrocarbons rich in car-

As it appears from this table, the fraction of 80 to 103° which one obtains by the pyrogenic distillation of the petroleum extract corresponds to an inter-

TABLE II.—COMPARISON OF THE QUALITIES OF ILLUMINATING OILS OBTAINED BY THE ORDINARY AND BY THE EDELEANU PROCESS.

		Illuminating Power. Photometric measurements at each hour with the Kosmos Burner 14. Illuminating Power in Hefner Units.									
Origin.	Refining Process.	Specific Gravity.	0	1	2	3	4	5	6	7	8
Bustenari	Ordinary process.....	0.818	7.2	7.1	7.1	7.2	7.1	7.1	7.1	6.7	6.7
	SO ₂ process.....	0.803	13.8	13.3	13.2	13.2	13.2	13.0	12.8	12.5	12.4
Cămpina	Ordinary process.....	0.812	10.4	10.1	10.1	9.9	9.9	9.9	9.9	9.9	9.9
	SO ₂ process.....	0.797	15.7	15.5	15.3	15.3	15.3	14.9	14.3	14.3	13.5
Moreni	Ordinary process.....	0.818	7.3	6.7	6.4	6.3	5.6	5.6	5.6	5.3	5.1
	SO ₂ process.....	0.805	13.5	12.8	11.8	11.2	11.2	11.2	10.9	10.8	10.8
Tustanovice	Ordinary process.....	0.799	13.8	13.7	13.1	13.1	12.9	12.9	12.4	12.0	11.7
	SO ₂ process.....	0.786	17.2	17.2	16.7	16.0	15.5	15.0	14.4	14.0	13.7
Grossny	Ordinary process.....	0.815	10.0	10.0	9.9	9.8	9.8	9.6	9.2	9.1	8.9
	SO ₂ process.....	0.806	15.4	15.0	14.7	14.3	13.9	12.8	12.4	12.1	11.8
California	Ordinary process.....	0.810	9.4	9.1	8.9	8.6	8.4	8.2	8.1	8.1	8.1
	SO ₂ process.....	0.798	14.7	14.3	13.9	13.5	13.2	13.0	12.8	12.8	12.6
Peru	Ordinary process.....	0.817	11.2	10.7	10.4	9.9	9.6	9.4	9.2	8.9	8.9
	SO ₂ process.....	0.807	14.3	13.8	13.6	13.6	13.5	13.5	13.2	12.6	12.1
Qualities of Illuminating Oil Brands Sold on the Market.											
Pennsylvania W. W.		0.7915	14.3	14.1	13.9	13.5	12.9	12.8	11.6	10.1	9.9
Pennsylvania St. W.		0.7995	12.8	12.2	11.9	11.8	11.2	11.0	10.2	9.7	9.2
Bakou Meteor		0.8087	11.1	10.8	10.8	10.6	10.6	10.6	10.2	10.0	9.9

bon. On account of their low burning capacity, they cannot be employed as burning oils; nevertheless, by dividing the extract into two products by redistillation, they become useful; the lighter part as turpentine substitutes or mixed with light benzine as a motor spirit of high efficiency, and the heavier as motor oil for Diesel motors. The extract is, therefore, as regards the possibility of turning it to account, at least equally as valuable as the distillate.

Further experiments have shown that the extract can be resolved by special means into the lower homologues of the aromatic hydrocarbons. By pyrogenic distillation the hydrocarbons contained in the extract are split up; and, besides a gaseous part, a large percentage of tar is produced. The latter is distinguished from tar derived from coal by its higher content of the lower members of the aromatic series of hydrocarbons.

Table III shows the product of gasification (pyrogenic distillation) of the extract as compared with other bituminous substances.

While coal tar hardly contains 2.6 per cent of aromatic hydrocarbons, the tar produced by pyrogenic distillation of petroleum contains between 15 to 23 per cent.

Among the fractions of this tar which distill above 200° a large quantity of naphthalene is found, which varies between 5 and 12 per cent, and of anthracene varying between 0.5 and 2.7 per cent.

The benzine which one obtains after the first redistillation of this tar is much purer than that which one obtains under the same conditions by redistilling coal tar. This result appears from Table IV which shows comparatively the composition of benzine obtained by the first redistillation of tar from the extract (treatment with dioxide of sulphur), and of that of the type of benzine used in commerce.

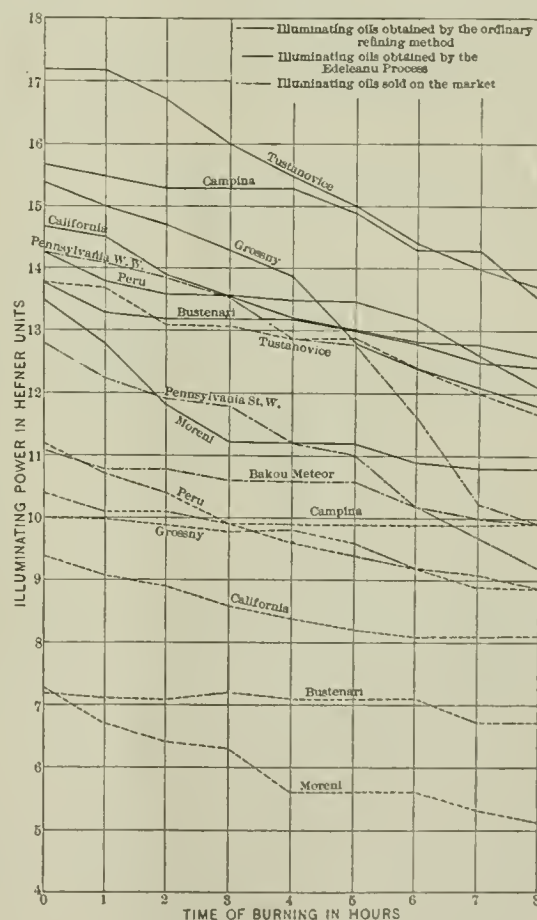


Fig. 4.—Comparison of Oil from Ordinary and Edeleanu Processes.

mediate quality which ranges between the 50 per cent type and the 90 per cent type, as sold in the market, and such as is obtained from coal tar by means of several redistillations. It must also be remembered that the benzine obtained by the pyrogenic treatment of the extract and of other products of petroleum is

totally free from thiophen and only contains a few impurities. By means of a little soda it is obtained perfectly pure.

Effect of Process on Distillates Containing Sulphur.—It is further to be noted that the liquid sulphur dioxide also possess the property of dissolving out

The following is a description of the treatment of a Roumanian distillate from Bustenari:

The dried distillate to be treated passes through filters charged with salt, is collected in a receiver, and finally reaches the distillation cooler after going through a cold-exchanging apparatus. The tempera-

TABLE III.—COMPARISON OF TAR EXTRACTS AND COAL TAR.
Composition of Tar Extract.

No.	Limits of Temperature ° Celsius.	Density at 15° C.	Products of Distillation	Per cent Calculated for tar.	Average Composition of Coal Tar according to Prof. Kramer. Products of Distillation.	Per cent.
1	80°—113°	0.8700	Benzène Toluène	13.3	Benzène et Homol	2.50
2	113°—140°	0.8700	Little toluène	...	Phénols	2.00
			With much xylène	9.1	Résidue	0.25
3	140°—250°	0.9870	{ a. Naphtaline	8.7	Naphtaline	6.00
			{ b. Hydrocarb. arom. liquids.	23.7	Heavy oil	20.00
4	250°—400°		{ a. Anthracène crude	1.0	Anthracène, Phénantrène .	2.00
			{ b. Anthracène oil	20.0	Asphalt	38.00
5	above 400°		Résidue	21.2	Coke	24.00
			Loss	3.0	Water	4.00

from crude distillates certain sulphur-containing constituents. For instance, by treating a Mexican distillate of 0.803 specific gravity and with a sulphur content of 0.6 per cent an oil is obtained which shows a percentage of sulphur of only 0.08 per cent and another oil of 0.79 specific gravity, with a sulphur content of 0.46, could be reduced to a percentage of sulphur of 0.04.

The process was first tested in a small experimental plant in the Vega refinery at Ploesti.

TABLE IV.—COMPOSITION OF COMMERCIAL BRANDS OF BENZENE.

Commercial Benzene.				Benzene from Extract 80°—113° C.	
Limits of Temperature, ° Celsius.	30 Per Cent.	50 Per Cent.	90 Per Cent.	Limits of Temperature, ° Celsius.	Per Cent.
80°	0	0	25	85°	0.0
90°	2	4	70	90°	13.4
95°	12	26	83	95°	48.0
100°	30	50	90	100°	74.0
105°	42	62	94	105°	88.0
110°	70	71	97	110°	96.0
115°	82	82	98	115°	98.0
120°	90	90	99	120°	99.0

The results obtained with this small experimental plant were entirely satisfactory and shortly afterward the construction of the necessary plant for carrying out the process on a large scale was undertaken by the firm of A. Borsig, of Tegel (Berlin). A refining plant was next installed in Rouen, and was followed soon after by the construction of a plant of similar size in Ploesti. The capacity of the plant at Ploesti, originally intended to treat up to 25 tons of distillate per day, was soon increased to 70 tons a day and the nature of the products is giving every satisfaction.

These trials were considered to demonstrate completely the practicability of the process on a large scale. One of the largest and most influential petroleum concerns has since ordered a plant with a daily capacity of 250 tons, and already an increase to 500 tons is being contemplated. There are now other large plants in course of construction for Galicia, Roumania, Borneo, India, etc.

ture of the distillate is first lowered in the cold-exchanging apparatus, and it is then further cooled in the distillation cooler itself until it reaches the desired low temperature. Similarly, the liquid sulphur dioxide coming from the vessel passes through a second cold-exchanging apparatus, where its temperature is reduced somewhat, and from thence to the sulphur dioxide cooler itself, where it receives the necessary final cooling.

The arrangement is shown in Fig. 5.

The distillate to about — 10° C. is now let into the lower mixer, a cylindrical vessel which is provided with level gauges, and in its lower part with gauge glasses, so that the reaction in the liquid may be accurately observed.

The introduction of the liquid sulphur dioxide into the mixer begins immediately. The sulphur dioxide is at first entirely absorbed by the distillate, without any appreciable change of the liquid. As soon as the distillate is saturated with the liquid sulphur dioxide, dark cloud masses begin to rise, and the color changes suddenly to a deep brown. This change of color is brought about by the separating out of the liquid sulphur dioxide loaded with the aromatic hydrocarbons, and depositing at the bottom of the mixer. There are now two sharply divided layers which can be distinctly observed through the level gauges. As soon as there is a certain quantity of extract formed, the drawing-off commences; at the same time further quantities of liquid sulphur dioxide are supplied to the mixer.

The extract is drawn by the extract pump through the cold-exchanging apparatus into the extract evaporator. In the cold-exchanging apparatus it meets the comparatively warm distillate flowing to the distillation cooler (as described above) by which its temperature is considerably raised. In this way the distillate receives a preliminary cooling and the extract a preliminary warming. The latter is then further warmed in the extract evaporator, which is provided with heating coils. This causes the rapid evaporation of the dissolved sulphur dioxide which flows directly into a

condenser, where it accumulates in the form of a liquid; it is then stored in the reservoir, from whence it commences its cycle afresh.

As soon as the greater part of the sulphur dioxide contained in the extract has been driven off, the evaporation is gradually brought to a stop. The final remaining portion of the sulphur dioxide is held very tenaciously by the extract, and cannot be driven off merely by the application of heat. In order to prepare the extract evaporator for a fresh charge, the extract with its still remaining small contents of sulphur dioxide is run into an auxiliary evaporator. Here, the balance of the sulphur dioxide is drawn off by a sulphur dioxide gas pump under continuous application

treatment with very small quantities of sulphur dioxide is advantageous in order to obtain a "water-white" color.

The exhaust steam from the steam engine which drives the plant is utilized for the heating of the evaporators.

While the evaporating process is still going on in the extract evaporator a new operation takes place, a freshly cooled distillate being admitted to the mixer and saturated with liquid sulphur dioxide, until again fresh quantities of extract settle out. By this time the evaporation in the extract evaporator is also finished and the apparatus emptied, so that the new operation is able to proceed without interruption.

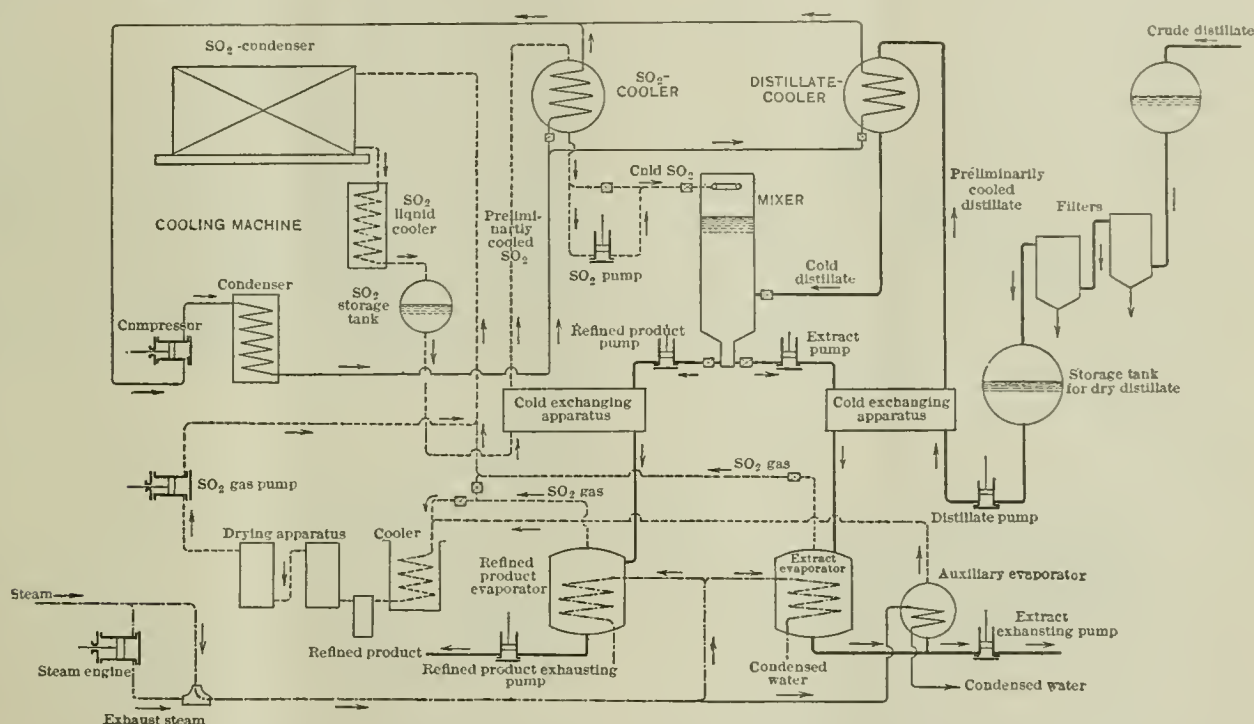


Fig. 5.—Plan of Refining Plant for Liquefied Sulphur Dioxide Process.

of heat, and sent to the condenser. This is continued until about 0.3 per cent still remains in the extract, when the latter is removed from the auxiliary evaporator.

The refined product is pumped through the second cold-exchanging apparatus into the second evaporator. It meets in the cold-exchanging apparatus the liquid sulphur dioxide flowing from the tank to the cooler, and is raised to practically the same temperature. In this way the liquid sulphur dioxide receives a preliminary cooling (just as in the case of the distillate). The refined product is then collected in the evaporator and undergoes a similar process of evaporation as the extract. By means of heat and continued suction the sulphur dioxide is almost completely removed, only about 0.1 or 0.2 per cent remaining; at which stage the refined-product evaporator is emptied.

The treated distillate, after being washed and neutralized with an alkaline solution, may be used as finished illuminating oil. In some cases subsequent

The cooling of the distillate and sulphur dioxide collected in the two cooling vessels is effected in the usual manner with the help of cooling coils, which form a part of a separately working cooling machine. The cold-producing medium enters the cooling tubes as a liquid, evaporates on account of the continuous low pressure produced by the suction of the compressor of the cooling machine, and abstracts from its surroundings, i. e., the distillate and liquid sulphur dioxide, the heat required for its evaporation. The vapor of this cooling medium is afterward sucked up by the compressor and led to the condenser of the cooling machine, where it is again collected in liquid form.

The method of working is shown graphically in Fig. 6. In this diagram it is shown how fresh distillate is continuously entering the system, and how it finally leaves the system split up into refined product and extract, and how the sulphur dioxide which effects the splitting up, is recovered with the exception of a

very small quantity, and is then used again for the process, making a complete cycle. It may also be seen that of the distillate put into the system nothing is lost; the products treated, viz., the volume of extract and the refined product, together are equal in volume to that of the original distillates.

As the sulphur dioxide performs a complete cycle, it cannot when once entering the system in a pure and anhydrous condition, give rise to any undesirable complications. It is well known that liquid sulphur dioxide is quite inactive toward metals, so that there is no fear of the apparatus becoming injured or destroyed in the course of time.

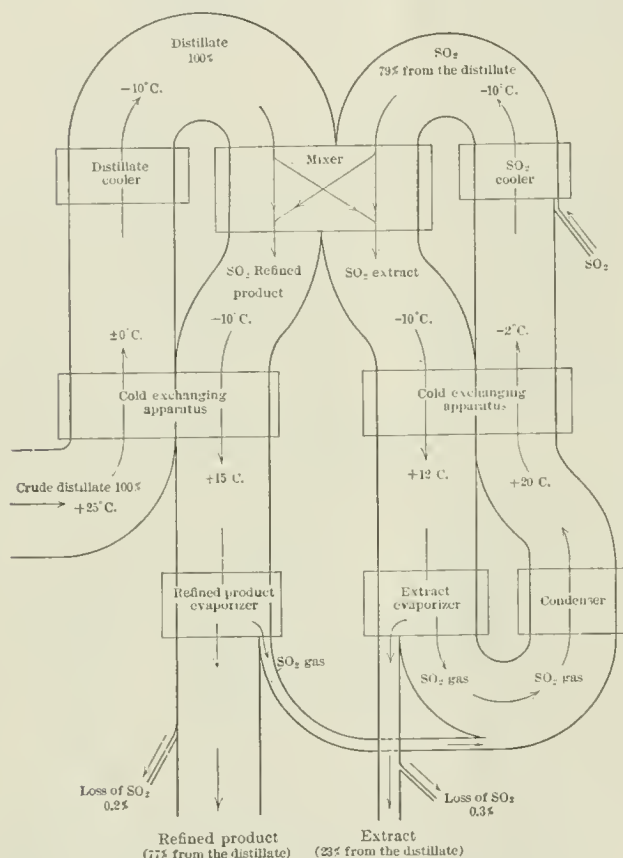


Fig. 6.—Plan of the Edeleanu Process.

However, great care must be taken that no moisture is introduced into the system with the distillate. The latter should, therefore, as mentioned above, pass through several drying filters before it enters the apparatus, so that all the moisture may be removed. Inasmuch as the system is perfectly airtight throughout, there is of course no possibility of moisture from the atmosphere penetrating into it.

The fact that the whole of the apparatus, pipes, valves, etc., are completely airtight is responsible for the fact that scarcely the faintest smell of sulphur dioxide is perceived in the plant. This is of the greatest importance for the welfare of the workmen who are in attendance at the plant.

The arrangement of the plant is such that from the operator's platform the colors which are placed high and the evaporators which are below, as well as the mixer in the center, may be watched and attended to.

As can be seen in Fig. 7, all the important pipes with their control valves are placed on a regulating table, so that the operator in charge of the refining process can take care of all the necessary regulating and connecting manipulations without leaving his place of observation.

Working Results.—The working results of a plant with an average daily capacity of treating about 65 tons of distillate per 24 hr., as were reached in the plant at Ploesti, are given in the following table:

Specific gravity of the crude distillate to be treated....	0.820
Average time of operation, minutes.....	68
Quantity of distillate treated at each operation, kilograms	3,115
Temperature in the mixer, degrees centigrade.....	-10
Specific gravity of treated product.....	0.8028
Specific gravity of extract	0.8691
Sulphurous acid left in the treated product, per cent..	0.16
Sulphurous acid left in the extract, per cent.....	0.36
Consumption of fresh steam per operation, kilograms..	1,200
Consumption of fresh steam per 1,000 kg. distillate, kilograms	385
Consumption of exhaust steam per operation, kilograms..	648
Consumption of exhaust steam per 1,000 kg. distillate, cubic meters	208
Cooling water used per operation, cubic meters.....	17.1
Cooling water used per 1,000 kg. distillate, cubic meters	5.5
Loss of sulphurous acid per operation, kilograms.....	17.5
Loss of sulphurous acid per 1,000 kg. (distillate), kilograms	5.6

From the above figures, the cost of treating a Roumanian Bustenari distillate can be calculated as follows:

COST OF TREATMENT IN A PLANT OF 65 TONS DAILY CAPACITY.

Cost of Plant:	Francs.
Machines and apparatus	130,000
Buildings, construction, freight, duty and other expenses	100,000
Total	230,000
Amortization and Interest:	
Amortization ...=10 per cent of 130,000	13,000
Amortization ...= 5 per cent of 100,000	5,000
Interest on the invested capital= 5 per cent of 230,000	11,500
Total	29,500

In 325 working days, at 65 tons per day, there will be 21,125 tons treated, so that the amortization and interest amount to Frs. 1,396 per ton, or per 100 kg.....Frs. 0.140

Maintenance, Labor, etc.:	Francs.
Repairs, working materials	6,000
Wages and salaries	8,000
Insurance, 1½ per cent.....	3,450
Lighting and heating	2,400
Drying salt, unforeseen expenses.....	3,000
Total	22,850

The cost of maintenance and labor, therefore, amount to Frs. 1.082 per ton, or per 100 kg.Frs. 0.108

Cost of Materials:	
There are required for each 1,000 kg. of distillate:	Francs.
385 kg. fresh steam at Frs. 3.50 per ton	1.35
208 kg. exhaust steam at Frs. 1.50 per ton	0.31
5.5 cbm. cooling water at Frs. 0.04 per cbm.	0.22
5.6 kg. sulphurous acid at Frs. 18.00 per 100 kg.	1.01

Cost of materials per 1,000 kg..... 2.89
Cost of materials per 100 kg.....Frs. 0.289

The total costs of treatment, therefore, amount toFrs. 0.537

or practically Frs. 0.54 per 100 kg. of distillate or 3.9 shillings per ton. It must also be taken into account that Frs. 18 per 100 kg. of sulphurous acid is a very high figure and refers to imported sulphurous acid. The cost of this material is very much lower when sulphurous acid is used which is produced in the country itself, or actually in the refinery.

COST OF TREATMENT IN A PLANT OF 500 TONS DAILY CAPACITY.

Cost of Plant:	Francs.
Machines and apparatus	1,100,000
Buildings, construction, etc.....	500,000
Total	1,600,000
Amortization and Interest:	Francs.
Amortization	
.... = 10 per cent of Frs. 1,100,000	110,000

5.6 kg. sulphurous acid at Frs. 10.00 per
100 kg. 0.56

Cost of materials per 1,000 kg. 2.44

Cost of materials per 100 kg. 0.244

The total cost of treatment..... Frs. 0.452 or roughly, Frs. 0.45 per 100 kg. of distillate or 3.26 shillings per ton. In this case, the cost of sulphurous acid is taken at Frs. 10 per 100 kg. sulphurous acid produced on the spot being reckoned. The cost of production is amply estimated throughout.

The above tables are based on figures actually obtained from the existing plants. It is, however, to be anticipated, that with further perfection of the work-

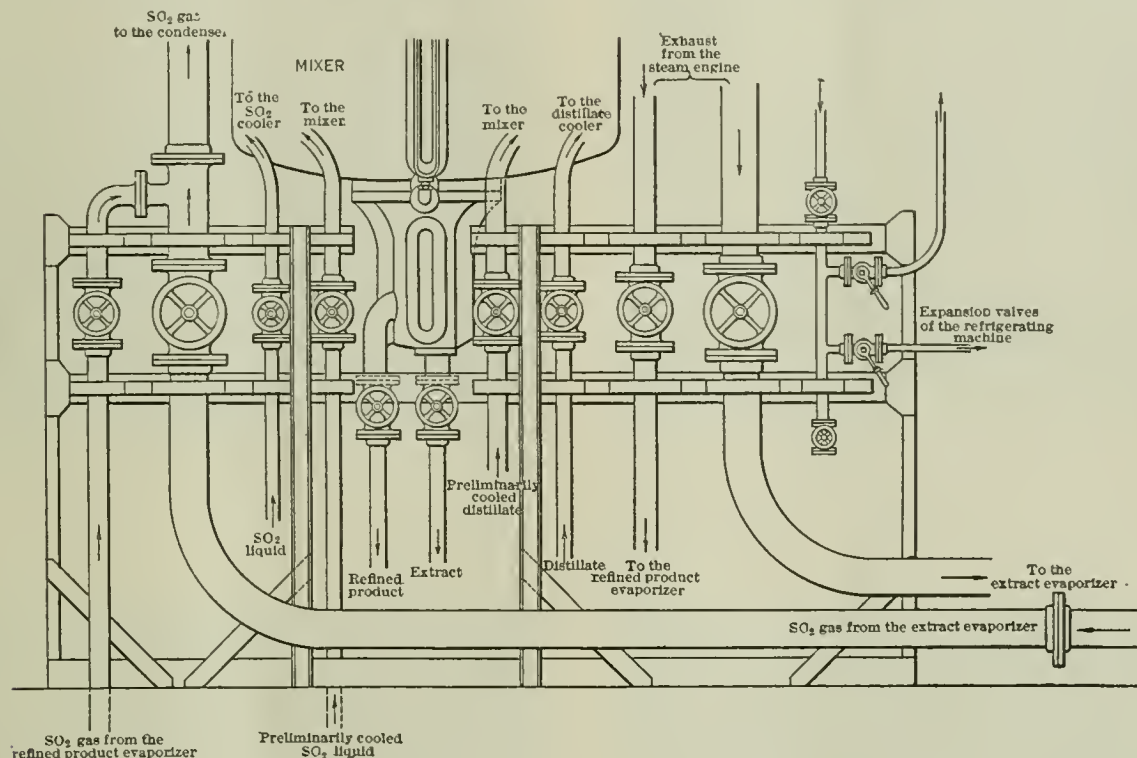


Fig. 7.—Diagram Showing Regulating Table in Apparatus Room.

Amortization	
.... = 5 per cent of Frs. 500,000	25,000
Interest on the invested capital	
.... = 5 per cent of Frs. 1,600,000	80,000
Total	215,000

In 325 working days, at 500 tons per day there will be produced 162,500 tons, so that the amortization and interest amount to Frs. 1.323 per ton, or per 100 kg. Frs. 0.132

Maintenance, Labor, etc.:	Francs.
Repairs, working materials	40,000
Wages and salaries.....	30,000
Insurance, 1½ per cent.....	24,000
Lighting and heating	10,000
Drying salt, unforeseen expenses.....	20,000
Total	124,000

Brought forward 0.132
The cost of maintenance and labor, therefore, amount to Frs. 0.763 per ton, or per 100 kg. 0.076

Cost of Materials:	Francs.
There are required for each 1,000 kg.	
of distillate:	
385 kg. fresh steam at Frs. 3.50 per ton...	1.35
208 kg. exhaust steam at Frs. 1.50 per ton.	0.31
5.5 cbm. cooling water at Frs. 0.04 per cbm.	0.22

ing of the process, the costs will be reduced even more.

In conclusion it may be well to summarize some of the chief advantages of this new process.

(1) The process makes it possible to obtain illuminating oil of good quality from the greatest variety of low-grade oils.

(2) The sulphur dioxide employed is cheap and practically all of it is recovered.

(3) Sulphur dioxide required for the process can even be obtained from the acid sludge available in the refinery in the manufacture of lubricating oils.

Since the beginning of September many large orders for chemicals and drugs have been received in Japan from Russia. These articles had formerly been obtained from Germany and more recently from England and the United States. Demand for iodic compounds, acetic acid, and other chemicals has been particularly large, and they are being exported through Kobe firms to Russia.

THE MICROSCOPIC STRUCTURE OF HIGH SPEED STEELS.

By H. B. PULSIFER.

It was at the suggestion of Professor H. McCormack of Armour Institute of Technology, that the author started a microscopic investigation of certain special steels which had served for thesis work in the chemical engineering department at the Institute. As the work progressed the clear and diverse structures which came to light proved the fertility of the early idea, justified all the trouble, and are presented here as a contribution to the rather meager store of photomicrographs now available relating to the high-speed steels.

The six steels selected were all from the usual commercial stock of dealers, and, according to the student analyses, had the chemical composition as seen in the table. (See this journal, July, 1914, p. 9)

TABLE I.

Sample.	A	B	C	D	E	F
Tungsten	13.69	13.63	12.99	16.82	17.88	17.56
Chromium	2.35	2.48	3.90	1.50	2.54	2.33
Carbon	.56	.70	.46	.60	.52	.58
Manganese	.06	.28	.07	.29	.43	nil
Phosphorus	.01	.05	.02	.03	.04	.03
Sulphur	.003	.008	.025	.015	.011	.009
Silicon	.18	.18	.13	.48	.28	.17

Some of the material came already in the annealed condition and soft enough to drill for the samples for the chemical analysis; the other samples yielded on very slow cooling after packing and heating in lime.

The material of sorts A and F came in little bars $\frac{3}{8}$ in. by $\frac{1}{2}$ in.; sorts B, C, D and E came in bars $\frac{1}{4}$ in. by $\frac{1}{4}$ in. and were cut to about 5-in. lengths. After the heating and quenching to which most of the bars were subjected a short end was broken off or else ground deeply and then broken, so as to be of suitable size for grinding, polishing and placing on the microscope.

The irregular structure of the little bars became conspicuous from the very first. In attempting to drill the samples for the chemical analysis a drill might go through a piece at one spot yet not be able to cut at all a quarter inch away. After the preliminary grinding on the wet emery wheel a considerable number of the pieces showed a soft envelope of rather uniform thickness about the whole exterior. Other pieces had a much diminished core of the harder structure or might have a few rounded spots of the hard structure at irregular intervals. Many pieces both to the eye and under the microscope showed uniform structure across the entire surface which was ground. The many cases of varied structure in the same piece have afforded some of the most interesting photomicrographs which we shall be able to present.

The heat treatment consisted in placing the bars in an electric carbon resistor furnace and bringing the temperature to the required temperature, holding for ten minutes then withdrawing a bar of each variety

and dropping same into a blast of air close in front of the furnace. One set of bars out, the temperature was increased to the next point, held ten minutes and the next set of bars quenched.

After this manner quenchings were carried out at the following temperatures: 920° C., 980° C., 1040° C., 1100° C., 1160° C., 1210° C., and 1280° C. With the six annealed pieces this gives a total of 48 specimens; one or more prints from each of these will comprise the structures to be presented.

The grinding of the specimens was effected on an emery wheel, using a side of the smaller bars and an end of the larger. After the roughing grind the surface was further smoothed with emery dust on canvas, tripoli on canvas and rouge on felt; vertical wheels used in all cases.

It was found that the usual scratch elimination process had a tendency to put the structures in the mixed specimens in so great relief that a flat field could not be obtained across a boundary zone with 500 diameters magnification. Accordingly, such specimens were given the best possibly surfacing on the stone and the least possible on the cloths; the desired result was obtained.

All specimens were first etched for 10 minutes in a solution of picric acid in alcohol, on removal and washing they were then merely dipped in 10 per cent aqueous nitric acid, again washed, immersed in alcohol, wiped with cotton and put in a dessicator.

If this treatment did not develop the structure sufficiently the pieces were placed in a strong solution of sulphurous acid until the features came clearly enough. The latter treatment was longer or shorter, depending on the specimen; some etched quickly, others were little changed over several minutes.

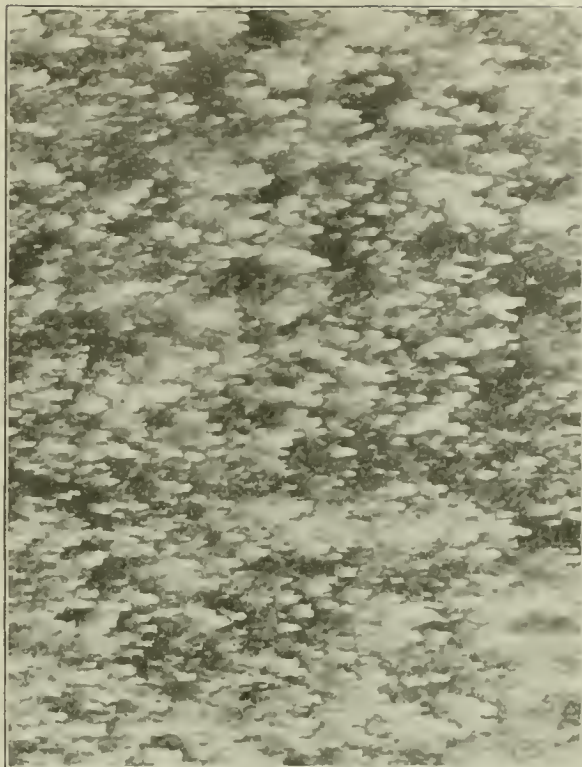
It is important to note that the extremely fine structures of this series of steels do not dry after etching without a very great susceptibility to oxidation. To the naked eye the surfaces are beautifully iridescent, instantly becoming banded in the moist condition. With a few of the prints this banding will be noticed; it is usually absent. When it does occur its origin and significance is thus explained.

Repolishing of the etched surface was practically always lightly done by rubbing wet on chamois with a very fine silver polish. This is not always necessary, but, as a rule, it improves the appearance.

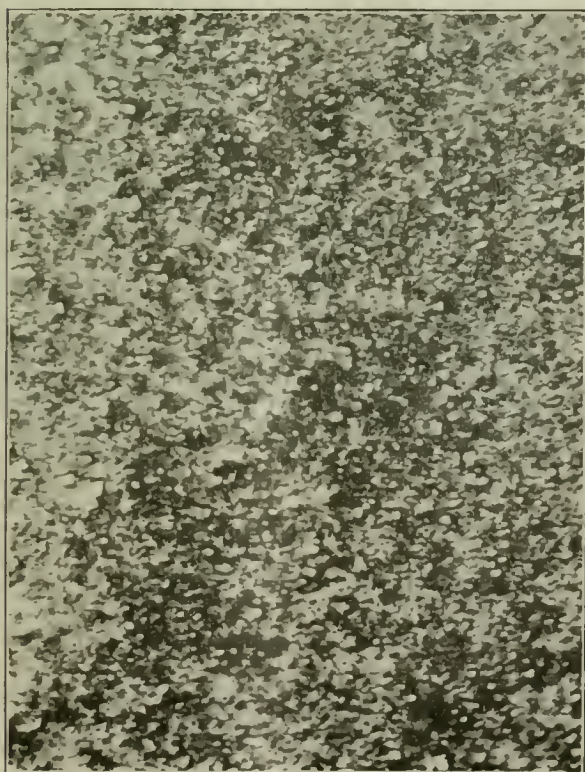
For the photomicrographs a Leitz inverted metalurgical microscope was used. Unless otherwise noted all magnifications are exactly 500 diameters; objective 6a; projection set at 61; plate on bellows extension at 61 cm.; green ground glass after the condensing lens. Diaphragm was varied to suit the brightness of the surface and the time also regulated between 15 and 60 seconds. Imperial plates and ortho-nonalation were both used; the author much prefers the latter variety, these giving by far the best negatives according to his experience. Hydroquinone developer



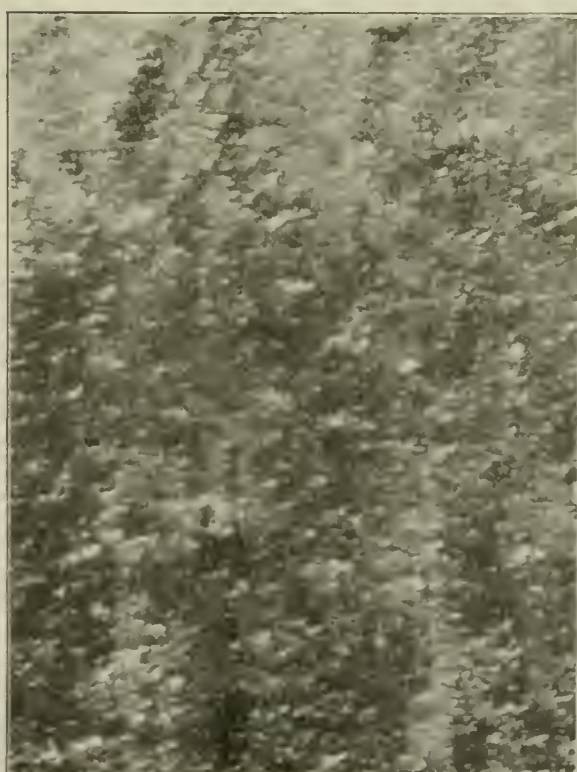
Specimen A.



Specimen B.



Specimen C.



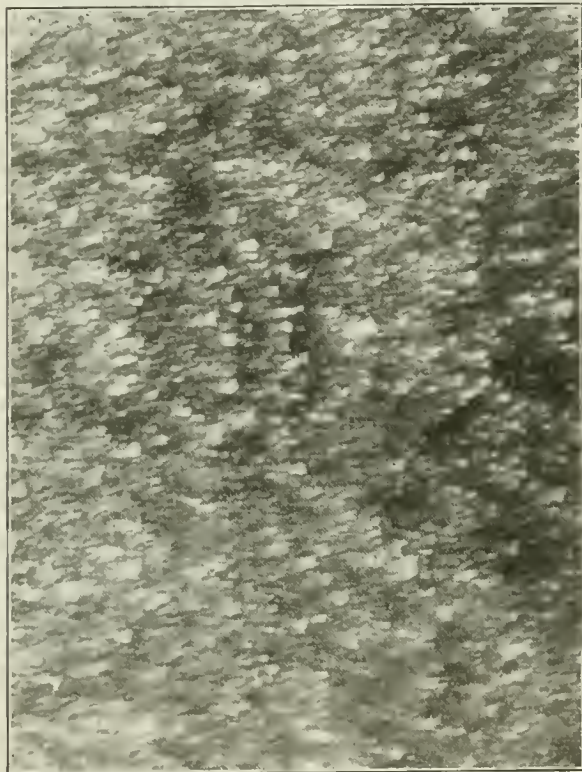
Specimen D.

served well for the plates and metol-quinone for the Axo F, Hard X paper used for all prints. The half-tone plates for the illustrations are made through a 150-line screen; on an enamel paper the halftone can-

scarcely go wrong if we refer to our white droplets as carbides.

The carbide droplets are not corroded by etching reagents. If a bit discolored the repolish brings them out bright and shining with their streamers too much in evidence on one side. Absent at times, the carbide persists to be found in nearly all fields examined; no matter how high the temperature of the quenching. Often the droplets are very minute and far between, seldom absent entirely.

The granular field of these annealed specimens is in all cases well differentiated and obviously derived from a similar structure typical of the quenched specimens which will be shown later. That the change is not uniformly completed is evidenced by the different degrees of etching attack, as between one specimen and another; the varying hardness, and abundant spots of closely packed and slightly etched areas. The granular appearance is in all cases, however, well established; the structure may thus be designated as peari-



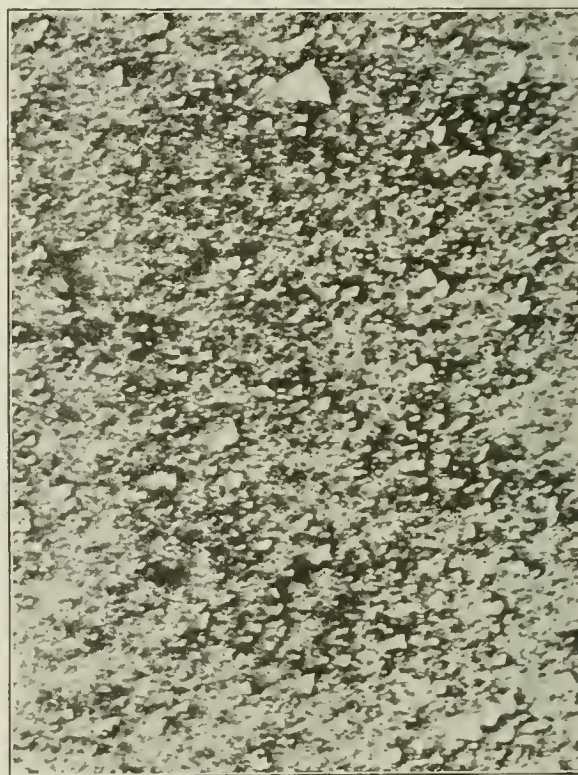
Specimen E.

not be distinguished from the print with the naked eye.

The six illustrations for this first installment are those of the annealed specimens, in order, A, B, C, D, E and F.

	Etching test.		Hardness.		
	Picric + Nitric.	SO ₃ .	Sclerescpe, 6 to 12 tests.		
	Strong attack.	Strong attack.	Low.	Mean.	High.
A	"	"	22	24	27
B	"	"	35	40	46
C	"	"	35	40	41
D	"	"	15	20	25
E	"	"	21	27	34
F	"	"	17	19	21

The six specimens of the annealed materials show rounded white droplets of a harder substance in an extremely fine, granular, easily corroded field. The droplets are doubtless carbide while the field has a pearlitic appearance, although of a finer texture than is common in the ordinary carbon steels. Arnold and Read, in a recent paper before the Institution of Mechanical Engineers (London, March 20, 1914) have described what is evidently the same material as the droplets as carbide of tungsten. They claim that at 11.5 per cent tungsten the iron drops out of the carbide and iron tungstide begins to associate with the tungsten carbide, increasing as the amount of tungsten rises above 11.5 per cent. Guillet* has long ago acquainted us with the double carbides in the chrome, tungsten and chrome-tungsten steels so that we can



Specimen F.

itic. Those who have studied such steels do not make very extended discussion of this point, probably assuming the obvious pearlitic nature of the general matrix.

According to the annual report of the Bureau of Mines, pig iron production in New South Wales in 1913 amounted to 46,563 tons.

*M. L. Guillet; *Revue de Metallurgie*, I, 263 (1904), and II, 350 (1905).

THE IDENTIFICATION OF ARTIFICIAL SILKS.*

By LOUIS J. MATOS, Ph. D.

Owing to the constantly increasing use of artificial silks and the consequent confusion arising in dye-houses and silk mills generally, due to the occasional, though unintentional, mixing of lots, it becomes a matter of some importance for the dyer or manager to be able to identify with certainty the several important kinds of artificial silks on the market. Where a dyer goes on from day to day with his work, and on one kind of silk, it is a matter of some consequence when he finds himself confronted with the problem of dyeing a new lot of different kind of silk that does not come out as expected, or which seems to offer difficulties during the dyeing.

Many instances are familiar to dyers where lots of mixed artificial silk have been sent to the dye-house, and inequality in the dyeing was not discovered until near the end of the operation, when it became a matter of great skill to bring up the shade of the indifferent skeins to the shade of the main lot. This condition could have been anticipated had the dyer been acquainted with the fact that the entire lot of silk was not of one kind.

From time to time there have been published tests and reactions with chemicals to be used in distinguishing the several kinds of artificial silks, but the practical application of which, in the dye-house or office, seems to offer some obstacles in the hands of those not actually acquainted with the details of making reactions. It seems that while the method of making the tests is simple enough, the greatest difficulty is in having the solutions or reagents properly compounded and in conducting the tests afterwards.

Simple descriptions alone do not seem to meet the case entirely. Of course, there is nothing to take the place of a practical demonstration of a testing method when carried out by one who is practically familiar with the proper sequence of the operations. On the other hand, many of the methods for fiber testing that have been published, while apparently intended for dyers and practical mill men, being those most concerned, are, as a rule, written for the chemist with some experience, as only such could possibly have the unusual reagents and apparatus, or even the apparently delicate manipulative skill, to handle both satisfactorily.

Without question, the most satisfactory means to identify artificial silk is to make use of the microscope, but as very few mills are equipped with this valuable instrument, and fewer still are proficient in making use of it, we will omit its discussion as applied to artificial silk and confine ourselves exclusively to the chemical or *wet methods* that experience has taught us

as being the most satisfactory. To identify artificial silk properly requires that the person attempting the work should have at hand a small set of chemical reagent bottles of not more than two-ounce capacity and with glass stoppers. Such bottles are not costly and may be obtained through a local druggist; the style known as "XX Tinctures" are admirably suited for the purpose. They are to be filled with the following reagents, which can be procured from a chemical supply house or prepared by a friendly pharmacist or chemical friend. The following constitutes the list and the methods for their preparation:

No. 1. *Glycerinated Sulphuric Acid.*

Pure glycerin 10 cc.

Distilled water 5 cc.

Add slowly with constant stirring, a few drops at a time, pure concentrated sulphuric acid—15 cc.

No. 2. *Iodo-iodide of Potassium.*

Distilled water 30 cc.

Potassium iodide 0.3 gr.

Iodide, an excess.

No. 3. *Chlor-iodide of Zinc.*

Distilled water 30 cc.

Fused chloride of zinc..... 1.75 gr.

Filter and add to clear filtrate Iodine to saturation.

No. 4. *Cold concentrated sulphuric acid.*

No. 5. *Half saturated chromic acid.*

No. 6. *A 40 per cent caustic potash solution.*

No. 7. *Copper oxide-ammonia.*

This is an important reagent in all fiber work. It should be made with great care by preparing a solution of copper oxide in ammonia to saturation, and passing through it a current of air freed from carbon dioxide, by first being passed through a solution of caustic potash.

No. 8. *Nickel oxide ammonia.*

Nickel sulphate in crystals..... 2 gr.

Water 30 cc.

Precipitate the nickel with caustic soda and filter; then dissolve the precipitate in a mixture of:

Concentrated ammonia 8 cc.

Water 8 cc.

No. 9. *Alkaline copper glycerin solution.*

Sulphate of copper..... 3 gr.

Water 30 cc.

Glycerin 1.75 gr.

to which is added a sufficient quantity of caustic potash solution to precipitate the copper and redissolve it.

No. 10. *Diphenylamine-sulphuric acid solution.*

Diphenylamine 1.57 gr.

Concentrated sulphuric acid..... 25 cc.

The operator should keep these bottles in a closet when not in use and at all times free from dust. The label, besides the name, should also have the formula written upon it.

The apparatus required to make the tests consists of a dozen small plain white butter dishes, a dozen small test-tubes of short length and not over half an inch

*From the American Silk Journal.

in diameter, and a spirit lamp or Bunsen burner to supply heat. There should also be at hand two small bottles or tubes containing red and blue litmus paper. The entire outfit is procurable under five dollars.

There are five kinds of artificial silk generally met with in commerce, as follows: Collodium Silk (Strictly nitro silks); Cellulose Silks; Viscose Silks; Acetate Silks; Gelatin Silks.

The first important test to make is to determine whether the silk under examination is made from gelatin or not.

Take one of the test-tubes, see that it is clean and dry inside, and place at the bottom of it a small tuft of the silk about the size of a small pea when rolled between the fingers. In the open end of the tube insert a piece of red litmus paper, bending the end over so that the strip will not slide down the tube. With a handle made of several folds of paper around the neck of the tube so as to permit one to hold it comfortably, place the closed end of the tube in the flame of the Bunsen burner or spirit lamp, giving the tube a slight to and fro motion until the fibers in the tube begin to char and vapors are seen to arise. When these vapors are observed to come out of the open end of the test-tube, note whether the color of the red litmus paper changes to blue. If such a change takes place it is due to the presence of ammonia gas resulting from the charring of the fibers and which could only come from gelatin silk. These vapors may also have the odor of burning horn or hair, which odor is further indicative of the presence of gelatin.

On the other hand, if the litmus paper does not change color, acid fumes may be present and are to be confirmed by repeating the test, but using *blue* litmus paper, and upon it turning red, indicates that the silk may be any one of the four above-named makes. To distinguish finally between the several artificial silks emitting acid fumes with heat, place two of the butter dishes side by side; in one, place some of the silk fiber and upon it pour some of reagent No. 1, and let soak for a few minutes, and then afterwards add a few drops of reagent No. 2. In the second dish put some of the fiber and a small amount of reagent No. 3, and note carefully what changes in color, if any, take place. If both samples show a distinct yellow coloration, the silk is *Acetate Silk*.

On the other hand, if the coloration is blue, the silk may be either *collodium*, *cellulose* or *viscose silk*, which is confirmed if the coloration shown in the second dish is reddish-violet. To differentiate between these three silks just mentioned, place a small tuft of the fibers in a dry dish and pour upon it a small amount of cold concentrated sulphuric acid (No. 4). If the silk dissolves rapidly, the specimen is either collodium or viscose silk; cellulose silk, *i. e.*, Pauly, Fremery, etc., dissolves slowly.

Confirmatory tests are made in test-tubes with the chromic acid solution (No. 5) in the cold, when these three silks dissolve gradually, and upon the tube be-

ing heated, dissolve quickly. When treated in the same manner with warm caustic potash solution (No. 6) these three silks, together with the acetate silk show a distinct swelling, while *gelatin silk* dissolves rapidly and completely.

The copper oxide ammonia test (No. 7) when applied in a test-tube first causes a swelling and dissolves collodium and viscose silks, but acetate silk swells without dissolving, and gelatin silk takes a bluish-violet coloration without dissolving.

The nickel-oxide-ammonia reagent (No. 8), when applied both cold and warm to a sample of artificial silk in the test-tube, causes a swelling of the fibers but without dissolving them. This applies to collodium, cellulose, viscose, and acetate silk, but not to gelatin silk, which latter takes a brown coloration without dissolving.

The alkaline-copper-glycerin solution (No. 9) has no action even after long boiling upon the first four silks above mentioned, but gelatin silk dissolves after a short time.

A convenient reagent for artificial silk is the concentrated sulphuric acid-diphenylamine solution (No. 10) which has been extolled as the one reagent for this class of work, but as a matter of fact its usefulness is limited exclusively to differentiate only the nitro silks from the others. With nitro silks of the Chardonnet type, it causes a distinct blue coloration, while the other silks remain uncolored. This diphenylamine reaction lasts but a comparatively short time, reaching its maximum intensity within five minutes after adding the reagent, when it gradually disappears.

In order to be in the position where one can absolutely and certainly pass judgment upon the identity of a given silk sample, the operator should have at hand a collection of true type samples obtained directly from the artificial silk manufacturers and to make the above outlined reactions repeatedly, systematically and with care. By care is meant not being too hasty in forming a conclusion, and to disregard and reject completely any test that one may have made, into which the element of doubt enters. With such a set of proved samples at hand and a set of reagents as above outlined, when unusual lots are received by the dye-house, or where silk is received from unfamiliar sources, its identity can be accurately determined.

The foregoing details refer to undyed artificial silk, but to identify dyed silk by chemical means requires that it should be stripped of its color, which is generally very easily accomplished by means of Hyraldite or some other equally efficient stripping agent.

The production of sulphite cellulose in Norway and Sweden for export and home consumption, including bleached pulp, during 1913 was about 951,000 tons (estimated), compared with 905,000 tons in 1912, and 764,000 tons in 1911. The production of sulphate cellulose, which was 171,000 tons in 1911 and 180,000 tons in 1912, is estimated at 205,000 tons in 1913.

RAW MATERIAL FOR PAPER PULP IN THE SOUTH.*

By VASCO E. NUNEZ.

A few figures will suffice to show something of the present status and growth of the paper industry in this country. In 1869 the value of the paper produced in the United States was roughly \$40,000,000; in 1899 it was \$127,000,000; and in 1909, \$268,000,000, an increase of 110 per cent in the last ten years for which statistics are available. In 1909 over 4,200,000 tons of paper of all classes was produced, approximately 100 pounds for every man, woman and child in the United States at that time. The capital invested amounted to over \$400,000,000, and the running expenses for the year were nearly \$240,000,000. The raw material used cost \$165,000,000, including the cost of 4,000,000 cords of pulpwood, more than half of which was spruce. From 1899 to 1909 the increase in the total amount of pulpwood used in this country was about 100 per cent, and during this period the increase in the consumption of domestic wood was but 35 per cent, while that of imported wood was 162 per cent. This means that the supply of pulpwood to meet the rapidly growing demand of the paper-maker is being imported in ever increasing proportion. The domestic supply is not keeping up with the demand. At the present time, approximately one-third of the pulpwood used in the United States is imported from Canada, and it is estimated that thirty years will see the last of what is now considered pulpwood timber in this country.

It is apparent from all this that in order to prevent the woodpulp and paper industry of the United States from taking wings and flying over to Canada something must be done to provide new sources of raw material. There are two obvious ways of doing this: First, to make use of new woods and of woods hitherto considered inferior for papermaking purposes; second, to make more extended use of fibrous wastes of manufacture and introduce new fibrous materials aside from wood.

In determining the value of a new fibrous raw material for papermaking a number of factors must be given careful consideration, and failure in any one requirement is usually sufficient to throw the material in question definitely out of the running. In the first place a large, durable and sufficiently cheap supply of the material must be available; the location of the supply must be such as to permit economical operation of the mill and marketing of the product; the material must be reasonably easy to collect and handle; it must not be too bulky, since otherwise the yield per unit volume would be unprofitably low; the cellulose content of the material must be at least 35 per cent and the other chemical constituents of the material of such nature as not to hinder its ready conversion

into pulp; and, finally, it must have a well defined fiber. It is at once obvious that wood fulfills these various requirements almost perfectly, and that the most logical approach to the solution of the problem under discussion is the search for new woods of suitable properties.

Along the lines of utilization of new or inferior woods, a great deal has already been done in an experimental way. The Forest Products Laboratory, United States Department of Agriculture, Madison, Wis., has found that hemlock, jackpine, balsam fir, and various species of Western fir can be made to serve as substitutes for the vanishing spruce in the manufacture of newsprint paper; Douglas fir is being used on the Pacific Coast, and redwood is considered a possibility in California. In the South, longleaf pine is receiving a great deal of attention.

As to fibrous materials other than wood, cotton stalks, corn stalks, bagasse, waste sisal and manila hemp fiber, the wild hemp of Colorado, and a large number of reeds, canes, straws, and grasses merit and have received consideration for papermaking, as have also cotton seed hull fiber and the flax straw of our northwestern States, though these two latter materials should not be considered as wood substitutes but rather as additional sources of rag fiber. A large number of these raw materials can be, and it is expected will be, furnished by many of the southern States.

Extracted sugar cane or bagasse has been the subject of considerable unsuccessful experiment on a manufacturing scale. Mills in Louisiana have operated for a short time on this material only to be abandoned. This should excite no wonder when the character of their raw material is considered. Bagasse resulting from the usual roll crushing extraction process is unfit raw material for paper for various reasons, the chief of which is the impossibility of producing a high grade, durable sheet without previous separation of the fiber and the pith of the cane. Arthur D. Little, Inc., have recently completed an extensive series of researches on the papermaking properties of bagasse from the Simmons sugar process. This process, as you are doubtless aware, is a radical departure from the usual sugarmaking practice. The cane from the field is shredded and dried, and the pith and fiber separated by air blast before extraction of the sugar. In the dry state the unextracted cane keeps indefinitely without the slightest fermentation (bales are now in our storage made in 1911), and may be shipped to any desired point for sugarmaking and papermaking operations. The fiber used by itself works up into various papers, and when mixed with woodpulp or other paper stock sheets of very desirable characteristics are obtained. Future development of the papermaking side of the process seems very promising.

Another waste material occurring in very large quantities throughout the South is the stalk of the cotton plant, for the use of which for paper a project

*From Paper.

is now on foot. It is evident that very great difficulties in collection of a supply of this material must be overcome; furthermore, experiments to date have been unsuccessful in producing paper of high quality, so that the value of the cotton stalk for papermaking is dubious. However, the question has not yet received the study which it demands.

A large number of southern reeds, grasses, and straws could be used for paper had they less severe competition than that of wood, and they will undoubtedly be so used to more or less extent when wood becomes less plentiful. At present some work is being done in Florida with saw grass; rice straw has also received consideration, and experiments at our mill with certain reeds gave generally satisfactory results.

The chief papermaking raw material of the South, however, and the one which is of the greatest present interest, is that which surrounds us on every side—longleaf pine. This wood, which outranks all others in commercial and industrial value, is too valuable to be worked directly into paper, and it is only the waste of the logging and milling operations that the papermaker can hope to touch. The amount of this waste, however, is too vast to be readily conceived. The total cut of yellow pine in 1910 was 14,000,000,000 board feet. It is estimated that 60 per cent of the total wood in the tree is wasted in the woods and at the mill, so that since the figure just given refers to output of finished lumber, the total waste wood amounted to 21,000,000,000 feet. This amount of wood is sufficient to make about 35,000 tons of paper a day, provided it could all be collected and used. The papermaker, however, is forced to be somewhat nice in the selection of the wood that he uses. He cannot use red heart, punky or partly rotten wood, nor wood that is badly charred, nor wood that is excessively knotty. He cannot afford to handle very small pieces, and he suffers some loss when removing the bark, due to the fact that a greater or less amount of wood immediately underlying the bark is usually removed at the same time. Making generous allowance for these losses, and for the unavailability of a large proportion of the waste wood in consequence of its location, we may safely assume that at least 10 per cent of the total waste is suitable and available for papermaking purposes. On this basis there is enough wood for the manufacture of 3,500 tons of paper every 24 hours. This would add about 25 per cent to the total production of paper in the United States.

Longleaf pine wood is well adapted for the manufacture of certain classes of paper. It is heavy; it possesses a strong, broad fiber averaging 4.28 millimeters in length, as compared to the fiber length of 2.8 mm. for spruce and 2.4 mm. for hemlock. The yield of pulp per unit weight compares favorably with that of other pulpwood, and the yield per unit

volume is higher than most. The chief disadvantage of the wood for papermaking is its high content of resinous matter, which precludes the application of the sulphite process for pulp manufacture, which, in point of cheapness of operation and ease with which the product may be bleached, is generally superior to the sulphate or soda pulp processes.

The two latter processes may be successfully applied to the pulping of longleaf pine, and it has been definitely proved that the sulphate process is superior for the purpose. The particular process which has been commercially adapted is the kraft sulphate process, the product of which is a tough, long-fibered, unbleachable, brown pulp excellently suited for the manufacture of kraft wrapping paper. By this process one cord would yield about 1,200 to 1,500 pounds of paper pulp. In the operation of this process the wood, after having been reduced to chips of suitable form and dimension, is fed to a steel digester which may be either stationary or rotating, and cooked for three to six hours under steam pressure of about 100 pounds, with a strongly alkaline liquor, containing as its principal ingredients caustic soda, sulphide of soda and sulphate of soda, or salt cake. After cooking, the chips, which are now thoroughly softened—the greater part of the noncellulosic constituents of the wood having been dissolved—are blown from the digester and the pulp thoroughly washed, and then screened to free it from splinters and unreduced particles. The pulp is then pumped to the beating engines, or hollanders, and after beating and subsequent refining in a Jordan or Marshall engine is run out into paper over a fourdrinier or sometimes over what is known as a Flying Dutchman machine. The chief feature of the latter is that several small, drying drums of the fourdrinier are replaced by a single drier of large diameter. The success of the process depends in a large part on the recovery and reuse of the chemicals used in the cooking liquor. The "black liquor" and washings of the pulp are collected, evaporated to a considerable extent, and passed to a rotary incinerator, where they burn to a so-called black ash containing the soda salts chiefly in the form of soda ash. This black ash is further incinerated and fused in a furnace called the melting furnace, and at this stage whatever loss of chemicals has occurred is sufficiently made up by the addition of salt cake (sulphate of soda). Chemical action in the melting furnace converts part of the salt cake into sulphide of soda. The melt is then dissolved in water, and the soda ash present converted to caustic soda by addition of quicklime. The liquor now contains its original constituents, namely: Caustic soda, sulphide of soda, and sulphate of soda, and is ready for use in cooking another lot of wood.

As already stated, longleaf pine seems particularly well adapted for the manufacture of kraft wrapping paper. Kraft was introduced into this country from

Sweden about ten years ago, and is the last word in wrapping paper. The paper largely used in former years for wrapping parcels was a comparatively heavy sheet made largely of sulphite spruce pulp. It was easily torn and expensive because a pound has so little covering power. When one buys wrapping paper, the consideration should be not, What does it cost a pound? but, What does it cost a square foot? Kraft costs less per square foot than many papers which it considerably exceeds in price per pound since, owing to its remarkable strength and durability, it may be made very thin and light. By reason of these properties it has almost driven the older wrapping papers from the market in the East and North.

The use of longleaf pine for wrapping paper has been dwelt upon because kraft is the only important variety of paper which has thus far been made successfully in a large way.

The other so called "yellow pines"—shortleaf and loblolly—are generally considered inferior to longleaf pine for papermaking purposes, but this opinion appears to be founded on scanty evidence since little work has been done toward their evaluation.

As you are all aware, four paper mills using longleaf pine have already been built and put into operation. Of these two are now idle, while the other two passed through a long period of trouble and tribulation before reaching a satisfactory operating basis. I am convinced, however, that these part failures are due not to the unsuitability of longleaf pine as a paper-making raw material but to other causes.

I believe that the longleaf pine district of the South has a rosy future as a papermaking territory. Fuel and raw materials are plentiful and inexpensive. Supplies are generally more expensive than in the North, but not excessively so. The climate is even, and fuel for heating purposes is practically unnecessary. Water is found in abundance, and is generally of excellent quality for industrial purposes. The freights to the northern markets are high, but by no means prohibitive, and the wonderful progress and advancement of the South are opening an increasingly important market close at home, while the Panama Canal will open up the markets of western South America and of the Antipodes. The papermaker is reaching out around him for new materials; he will reach into the South, into Louisiana, and will turn its present waste materials into a new source of wealth and profit.

An effort is being made by the Bureau of Agriculture at Manila to raise the standard of quality for the copra produced in and exported from the Philippine Islands. For some time it has been a matter of no little concern that it has brought a uniformly lower price than that produced in other countries. Moreover, the demand for the low-grade Philippine copra has never been as brisk and constant as that for the high grades produced in other countries.

CUBAN SUGAR INDUSTRY.*

The treaty of reciprocity between the United States and the Republic of Cuba, which was negotiated in 1902, allowed a preference of 20 per cent in the duty on Cuban sugar entering the United States. Since that date Cuba has entered upon a period of development that has exceeded the predictions of the most optimistic. Vast new areas of land have been brought under cultivation, new mills have been erected, old mills have been remodeled and improved, and projects are on foot for many additional mills to be built in the near future. So great has been this recent development that it can safely be said that if the present activity continues Cuba will be in a fair way of becoming the largest producer of sugar in the world.

The relations between Cuba and the United States have been so close during the last few years that it is interesting to observe to just what extent American capital has invested in the Cuban sugar industry. A careful estimate of this investment in mills, lands, railroads, and other equipment devoted exclusively to the industry, but not including mortgages, gives a total of \$54,000,000. In this estimate, however, are included a few companies which were organized in the United States and hold charters granted by different states, but whose stock is owned by persons other than Americans. Their investment amounts to a very small percentage of the whole. The distribution of this total investment through the different provinces of the island is as follows: Pinar del Rio, \$750,000; Habana, \$3,000,000; Matanzas, \$5,750,000; Santa Clara, \$14,500,000; Camaguey, \$4,700,000; and in Oriente, \$25,300,000.

There are in the island at the present time 173 active mills, of which 34 are wholly American owned and 2 partly controlled by American capital. Another interesting fact is that American-owned mills produce nearly 35 per cent of the total sugar output of Cuba. In Pinar del Rio they produce over 22 per cent; in Habana, 15 per cent; in Matanzas, 14 per cent; in Santa Clara, 26 per cent; in Camaguey, 58 per cent; and in Oriente more than 70 per cent. From this statement it can readily be seen that in the Provinces of Camaguey and Oriente the sugar output was largely from American mills, and, on account of the American mills now building and being planned in those provinces, these percentages will be increased still further within the next two years. Sugar in western Cuba has about reached the law of diminishing returns in agriculture, but the prediction is that eastern Cuba—Santa Clara, Camaguey, and Oriente Provinces—will continue to develop and expand until restricted by the lack of available land or until some unforeseen disaster overtakes the industry.

The impetus given the industry by the recent high prices and the favorable outlook for a continuance of

*From Daily Consular and Trade Report

at least a very remunerative price in the future has drawn the attention of many American capitalists to the profits in this field of endeavor; and in view of this interest it would seem that a brief description of the methods of culture and the cost of production, together with an estimate as to the cost of establishing a complete sugar estate in Cuba, might be of assistance. With this object in view the writer has collected, from planters, engineers, and investors in the industry, data bearing on the cost of production and the profits to be expected. It must be stated, however, that these figures are only approximate and many factors tend to make them vary, such as the location of the plant, price of labor, and whether European or American machinery is used, but the endeavor has been to be very conservative in the estimate as a whole.

In the first place, it can be stated that perhaps the two most important items to be considered are the fertility and adaptability of the land and the accessibility to transportation facilities. Provided that suitable land can be obtained, the ideal location for a modern mill is on or very near a good harbor, where ships can come up to its own dock. It should have its own railroad to carry the cane from the fields to the mill and to transport the sugar from the mill to the dock. This reduces to a minimum the cost of important machinery and supplies and of shipping the products of the mill.

Let us take as a basis a sugar estate which will produce 100,000 bags of sugar of 320 pounds each per annum. The amount of land for all purposes—fields, roadways, pastures, timber tracts, sites, etc.—should be about 20,000 acres, and good land of this character would cost \$6 to \$10 per acre, according to fertility of the soil and nearness to transportation facilities. The total first investment for such an estate would be about as follows:

20,000 acres of land, at \$10.....	\$200,000
Clearing and planting 5,000 acres, at \$50.....	250,000
Oxen and carts.....	60,000
Railroad and equipment.....	260,000
Wharf	40,000
Sugar mill and house.....	800,000
Office, store, dwelling, hospital, and barracks.....	40,000
Working capital	50,000
Total	\$1,700,000

Two general systems of growing the cane are in vogue in Cuba—the “colono” system and the “administration” system. The first contemplates the ownership of the land and equipment by the mill, money being advanced to “colonos” or tenants to grow, cut, and deliver the cane to the company's railroad, a percentage of the sugar extraction being returned to the tenant in payment for his work. In many instances the “colono” owns his land and equipment, and in such cases the basis of settlement is different only in that the percentage returned to him is larger. These percentages vary according to locality and the number of mills competing for the cane, but it probably averages about 5 per cent of the cane actually delivered to the

mill or the company's railroad. That is, for every 100 arrobas (arroba = 25.3664 pounds) of cane delivered to the mill the colono receives 5 arrobas of sugar or the market price for the same.

The second method, that of “administration,” is one in which the company owns the land and either does the whole work through its own employes or lets the different branches of the work out to contractors who perform the work under the supervision of the company's representatives. One class of contractors cleans the cane rows, another cultivates the crop, another cuts and loads the cane on the cars, etc. This seems to be the preferred method, and this is the one upon which the figures of this report are based.

In Oriente Province the average cost by contract of clearing land, fencing, making roadways, plowing, planting, and cultivating cane to maturity (12 to 14 months from planting) is \$50 an acre. The cane once planted in new and what is considered good sugar land will produce an average crop of 30 tons per acre per annum for a period of 10 years, after which time it would have to be replanted; and the cost of cultivation per year would be about \$15 per acre.

Taking these general figures as a basis, it would be necessary to plant the first year 5,000 acres of cane, which, at an average of 30 tons per acre, would produce 150,000 tons of cane per annum. Allowing a “rendimiento” or sugar extraction from the cane of 10 per cent, would give a production of 96° raw sugar of 15,000 long tons, or 33,600,000 pounds in all. The average net price for Cuban raws f. o. b. Cuba for the past 10 years, but but not including the high prices of 1911 and 1912, was 2.25 cents per pound. It must be stated here, however, that the high prices of 1911 and the favorable outlook as to future prices will considerably raise this average. This production of raw sugar would give approximately 1,000,000 gallons of molasses, and the price for which this could be sold would be about 3½ cents per gallon f. o. b. Cuba. Thus the following statement shows the gross annual income to be:

33,600,000 lbs. 96° raw sugar, at 2¼ cts.....	\$756,000
1,000,000 gals. molasses, at 3½ cts.....	35,000
Total income	\$791,000

In such a mill located near the coast, with no railroad freight to pay on its product and with efficient management, it is safe to say that the cost of producing this amount of sugar, including cultivation, harvesting, transporting the cane to the mill, railroad operation, mill operation, administration, maintenance, depreciation, insurance, taxes, and all other operating expenses, would not exceed \$550,000, or at the rate of 1.6 cents per pound. The difference between the gross income and the total annual cost would therefore be \$241,000, or slightly in excess of 14 per cent on the investment of \$1,700,000.



METHODS OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR INSTITUTE OF TECHNOLOGY.

A. Analysis of Raw Rubber.

Sampling. It must be emphasized first that sampling is an operation which requires the utmost care. Naturally the broad principles governing sampling in general will be observed. The sample must be taken from as many places as possible, and to be thoroughly representative of the bulk a large sample should be taken first, mixed, and again sampled. But it is necessary to remember that rubber is not an easy substance to sample. Variations can easily exist, even between adjacent portions of a sheet; consequently it is as well to be over-careful in the matter. Since accurate sampling is a precursor of all sound analysis, the greatest attention should be devoted to this point, and control experiments should be made to determine whether the chosen method of sampling is actually effective.

Moisture. The next determination necessary is that of moisture. This should always be estimated as the presence of more than a certain amount is apt to cause trouble; it leads to "porosity" of the manufactured article. This appears as small pores in the interior, after vulcanization, and is frequently to be attributed to moisture.

The estimation of moisture can be performed by several methods. Drying in vacuo, over sulphuric acid, is accepted as the standard. The finely divided rubber (rolled or cut with sharp scissors) is placed in a desiccator over sulphuric acid, and dried till the weight is constant. As Korneck has pointed out, twenty-four hours should elapse between the last two weighings. The process may require a number of days. It may be noted that good sulphuric acid must be used (evolving no acid fumes) and must be changed at frequent intervals. The process can be accelerated, as Ditmar recommends, by warming to a moderate temperature in an evacuated tube.

Other methods are more convenient for control purposes. Thus drying may be performed in a stream of coal gas at 100° C. It is simplest to have a water jacketed oven provided with an air condenser. A close-fitting, gas-tight door should be provided, which can be screwed or bolted up. Through this oven is passed a stream of gas, which may be used for heating afterwards. If the gas supplied is not pure, it may be necessary to wash it first, drying it afterwards. For control purposes, however, the gas need scarcely be specially dried unless it has been washed. There are two possible errors in this method. Rubber possesses

the property of absorbing gas, and thus the loss on heating may be less than the true value, or may even change into a gain on heating. In these cases a correction may be established by comparison with vacuum drying. Since drying for control is done to a certain fixed limit, it is not strictly essential to obtain absolute values so long as the results are concordant. It has been stated that the method ought to be discarded, since the illuminating constituents of the gas are retained by the rubber. This statement may be correct enough from an academic point of view, but the works chemist requires his results in a reasonable time, and if he can obtain results by gas drying sufficiently close for many requirements, he may still use the method, occasionally checking it by the vacuum method.

Estimation of Resins. Resin is almost invariably estimated in modern practice by extraction with acetone. Acetone extraction is as follows:

Two grams of rubber are wrapped in extracted cheese cloth, and the gross weight noted. It is extracted with acetone in a modified Wiley-Soxhlet extractor. The cheese cloth and the rubber are removed from the extractor and dried in a stream of hydrogen for five hours at 90° C. The loss is acetone extract, uncorrected. The acetone is removed from the extracted matter and the residue saponified with alcoholic potash. The alcohol is removed and the residue transferred to a separating funnel with water and ether. The unsaponifiable matter is thoroughly extracted, the ether layers are collected and washed with water, and the ether distilled off. In the analysis in question the unsaponifiable matter was not dried to constant weight, but was dissolved in alcohol and the waxy hydrocarbons frozen out with an ice and salt freezing mixture. After filtering off the insoluble waxes, they were dissolved in chloroform, transferred to a weighed beaker, the chloroform removed and the residue dried at 90-100° C. This residue is called the resins.

Determination of Insoluble Matter. It has been suggested by Ditmar and others that insoluble matter should be estimated directly by weighing the residual material filtered off from a more or less dilute benzene solution of the rubber, but, in my opinion, it may be estimated more conveniently indirectly. This operation is best carried out on the residuum from the acetone extraction, but in the case of sticky rubbers it is more convenient to work on the original sample. The method I apply is as follows: About ½ to 1 gram of fresh extracted material is accurately weighed and is then treated in a narrow 200 cc. measuring cylinder

with 200 cc. of benzene. The cylinder is shaken at intervals but the analyst must use his judgment as to when "solution" is complete. Two or three days are generally ample for this purpose. The liquid is allowed to settle over night and in the majority of cases a considerable volume of absolutely clear fluid above the finely divided insoluble matter is then available. An aliquot portion (20 to 50 cc.) of clear liquid is then pipetted off, evaporated on the water bath, and the residue then dried and weighed. The difference between the weight of the dried residue and the equivalent weight of the original sample obviously represents insoluble matter. The great advantage of this process over the processes in which insoluble matter is directly weighed, lies in the fact that it is extremely difficult to wash out all the rubber from the insoluble matter, and that a small quantity of rubber remaining on the filter or in the filtering tube may obviously lead to very grave errors.

Estimation of Nitrogen. Nitrogen is estimated by the usual Kjeldahl process: 1-2 grams rubber are placed on a 500-600 cc. kjeldahl flask; 20 cc. of a mixture of 3 vols. conc. and 2 vols. pure fuming sulphuric acid are added, together with one drop of mercury. Heating is continued on a sand bath till the solution is clear and completely colorless. In the presence of iron compounds the liquid is occasionally faintly yellow. After coloring the liquid is diluted with 250 cc. of water, washing down the flask. When again cool, 80 cc. of caustic soda (sp. gr. 1.35) (free from nitrates) are added, and as much potassium sulphide solution (40 grams commercial salt per liter) till all the mercury is precipitated and the liquid appears black. 25 cc. may be required.

A little zinc powder is added and the flask is rapidly connected with the distillation tube. The liquid is distilled till about 100 cc. have passed over into N sul-

phuric acid. The excess of acid at the end of the operation is determined by titration with N baryta,

using methyl orange. The nitrogen is calculated from the ammonia evolved.

One per cent nitrogen is usually considered to be equivalent to 6.25 per cent protein, when working on washed rubber. Unwashed rubber contains bodies richer in nitrogen.

Estimation of Ash. Ash is estimated by charring about 2 grams of rubber in a porcelain or platinum crucible, best in small pieces at a time, and gently igniting the residue. To prevent the rubber catching fire it is advisable to place the crucible in a hole cut out of any asbestos sheet so that the gas flame cannot set fire to the volatile products. The carbon can readily be burnt off at a gentle heat in the muffle. Good washed rubber does not contain much ash. In para it

may be as low as 0.2 per cent. A qualitative examination may be made. The following are frequently present: Ca, Mg, Fe, phosphates, sulphates, etc. It may be possible to draw some conclusions as to the origin of the rubber from the elements present in the ash.

B. Analysis of Mechanical Rubber Goods and Rubber Insulation.

Ash. One gram of finely ground rubber is extracted with acetone for 5-7 hours to remove free sulphur. It is then ignited in a small porcelain crucible, care being taken to have the temperature as low as possible to avoid overheating and decomposition of mineral fillers. The crucible is cooled and weighed. The residue is called ash. No correction is made for the sulphur present in the ash. Ignition is preferably made in an electrically heated muffle furnace.

Total Sulphur. One-half gram of rubber is placed in a porcelain crucible of about 75 cc. capacity, covered with 15 cc. of conc. nitric acid saturated with bromide, and allowed to stand over night. The next day the crucible is heated on the steam bath until the nitric acid and the bromide have evaporated. Five grams of a mixture of equal parts of potassium nitrate and sodium carbonate are added, and mixed thoroughly with the rubber, using a few drops of water. The mixture is dried and then fused over a gasoline burner. The fused melt is extracted with hot water and filtered. The filtrate is made faintly acid with HCl heated on steam bath, and barium chloride added to the hot solution. After standing overnight, the precipitated barium sulphate is filtered off and determined as usual.

Acetone Extraction. Two grams of rubber are wrapped in extracted cheese cloth and the gross weight noted. It is extracted with acetone in a modified Wiley-Soxhlet extractor. The cheese cloth and the rubber are removed from the extractor and dried in a stream of hydrogen at 90° C. for five hours. The loss is acetone extract, uncorrected. The acetone is removed from the extracted matter and the residue saponified with alcoholic potash. The alcohol is removed and the residue transferred to a separating funnel with water and ether. The unsaponifiable matter is thoroughly extracted, the ether layers are collected and washed with water, and the ether distilled off. In the analysis in question the unsaponifiable matter was not dried to constant weight, but was dissolved in alcohol and the waxy hydrocarbons frozen out with an ice and salt freezing mixture. After filtering off the insoluble waxes, they were dissolved in chloroform, transferred to a weighed beaker, the chloroform removed and the residue dried at 90-100° C. This residue is called "waxy hydrocarbons."

In determining the sum of waxy hydrocarbons it should be noted that all unsaponifiable matter may not be waxy hydrocarbons. A 30% para rubber compound will have about 0.5% unsaponifiable matter due to rubber resins soluble in acetone.

The water solution from the above ether extraction

is heated on steam bath to remove dissolved ether, bromide is added, and the solution heated for several hours. The solution is then made acid with HCl and filtered. The sulphur is determined in the filtrate with barium chloride in the usual way.

The sum of the waxy hydrocarbons and free sulphur, deducted from the acetone extract uncorrected gives the corrected acetone extract value.

Rubber. The difference between 100% and the sum of the acetone extract corrected, ash, total sulphur, and waxy hydrocarbons, is called "rubber by difference."

In certain classes of mechanical rubber goods it is advisable to make a quantitative analysis of the ash to determine the quantity and kind of fillers which have been used.

The kind of materials which will be estimated are magnesium, zinc and antimony. For the estimation of these minor constituents five grams of the rubber should be prepared as directed under "Ash Determination." The residue is dissolved in aqua regia evaporated nearly to dryness, taken up with hydrochloric acid, and the magnesium, zinc and antimony estimated as follows:

The hydrochloric acid solution is heated to about 80° C. Hydrogen sulphide is passed until the antimony is precipitated as a sulphide. This precipitate is removed by filtration, washed with water containing hydrogen sulphide, and then the filter paper containing the precipitate is placed in a Kjeldahl flask with 10 grams of potassium sulphide and 25 cc. of conc. sulphuric acid, and digested until all the material has passed into solution. The boiling is continued until fumes of sulphur trioxide are copiously evolved. The antimony should now be in solution as a sulphate and is estimated by titrating with potassium permanganate solution which has been standardized against C. P. antimony. The permanganate solution should be about one-tenth normal.

The filtrate from the antimony precipitation is boiled for some time to expel all the hydrogen sulphide. It is then brought to practical neutrality by the addition of ammonia and sodium hydrogen phosphate is added to precipitate the zinc as zinc ammonium phosphate. Once this precipitate starts to form, the solution should be boiled and stirred until the zinc ammonium phosphate assumes a granular condition. It is then filtered on a weighed Gooch crucible, ignited and weighed as zinc pyrophosphate.

The filtrate from the zinc precipitate is made strongly alkaline with ammonia and allowed to cool and stand for 12 hours or more. Magnesium is precipitated as magnesium ammonium phosphate and is filtered on a weighed Gooch crucible, is ignited and then weighed as magnesium pyrophosphate.

Storage and Time of Use. Wherever possible, each primary step in the procedure of analysis should be begun within one day of the time of grinding and finished as rapidly as possible. Where this is imprac-

ticable, the sample should be stored in a cool dark place, in vacuo of at least 26", or in an atmosphere of dry hydrogen or nitrogen.

The temperature of the sample shall not be raised appreciably above the normal during the grinding or due to the grinding.

METHODS FOR DETERMINING THE MELTING POINTS OF ASPHALT.*

By J. G. MILLER and P. P. SHARPLES.

SUMMARY.

Melting point determinations were made on a variety of asphalts by the cube method in oil, cube method in air (Hubbard), cube method in air (Barrett), and by the ring-and-ball method as practiced under five different specifications.

The methods for determination of the melting points of coal-tar pitches have been practically standard for a number of years. What is known as the "half-inch cube method in water"¹ is the recognized standard for the determination of the melting point of pitches of a melting point below 170° F. The attempt has been made to adapt the method to higher melting

TABLE 1.—COMPARISON OF HALF-INCH CUBE METHODS.
Size of Beaker, cc. Temperature at start, deg. Fahr.

Method.	Bath.	Apparatus.	Size of Beaker, cc.	Temperature at start, deg. Fahr.
Oil-bath, Barrett Mfg. Co.	Cottonseed Oil	One beaker	600	60
Hubbard	Air	Two beakers	Air, 300 Cottonseed oil, 800	77
Air-bath, Barrett Mfg. Co.	Air	Special Copper Oven		Normal

NOTE.—In all methods the specimens are ½-in. cubes, and are suspended at a height of 1 in. from the bottom of the apparatus; the suspending wire is of copper, No. 12 B. & S. gage; the rate of heating is 9° F. per minute; and the melting point is taken when cube touches the bottom of the apparatus.

points by substitution of a cotton-seed oil bath for the water bath, but the results have not been wholly satisfactory. The same methods applied to asphalts have not proved satisfactory owing to the low range of temperatures within which the method is adaptable; also because some asphalts have a specific gravity below that of the liquid bath.

Hubbard² has proposed a method which removes the difficulties encountered, both for the higher melting-point, coal-tar pitches and for the asphalts. The method, however, has not been widely adopted, and the asphalt manufacturers quote melting points by the ring-an-ball method.

In the laboratories of the Barrett Manufacturing Co. a method³ similar in principle to Hubbard's method has been adopted. This also obviates the difficulties

*From a paper presented at 17th annual meeting of American Society for Testing Materials.

¹S. R. Church, "Methods for Testing Coal Tar and Refined Tars, Oils and Pitches Derived Therefrom," *Journal of Industrial and Engineering Chemistry*, Vol. 3, No. 4, p. 227 (April, 1911).

²S. R. Church, "Dust Preventives and Road Binders," p. 351, John Wiley and Sons, 1910.

encountered in determining the melting point of hard coal-tar pitches and asphalts by the "half-inch cube" method.

Tables I and II show the results of tests of the half-inch cube method and the ring-and-ball methods.

The great discrepancies observed between the melting points as determined by the ring-and-ball method in the above-mentioned laboratories and the melting points given by the companies furnishing the asphalt led to an investigation of the method. It was found that the method as employed in different laboratories differed essentially in details, especially in the dimensions of the apparatus and the rate of heating. As the rate of heating is known to give wide variations

in results, the different methods were made comparable by adopting the widely used rate of 5° C. per minute. The results with different asphalts by the different methods are given in Table III.

The necessity for standardizing the ring-and-ball method is very clearly shown by the comparison of the results from the apparatus of the Chicago laboratory of the Barrett Manufacturing Co. and that of the Standard Oil Co. The very surprising difference of 25° F. was brought out, which is as much as the difference between the Hubbard method and the ring-and-ball method of the Standard Oil Co.

It is also to be noted that the cube methods cannot be compared with the ring-and-ball method even by the introduction of a factor, since the relative difference depends on the kind of asphalt.

In Table IV is shown the effect of using a heavy wire in the half-inch cube method.

Conclusions.—The cube method in oil has not proved satisfactory in the determination of asphalt melting points.

The cube method in air, as specified by Hubbard, has proved very satisfactory.

The ring-and-ball method would prove an acceptable and easy laboratory method, but no satisfactory concordant results can be obtained unless the method is thoroughly standardized.

TABLE IV.—EFFECT OF USING A HEAVY WIRE IN THE HALF-INCH CUBE METHOD OF TEST FOR ASPHALTS.

Material and Method.	Melting Point, Deg. Fahr.		
	No. 12, B. & S., 0.0808 in. diam.	No. 12, Stubbs, 0.109 in. diam.	Difference
Atlantic Asphalt, Hubbard Air-Bath Method	250	254	4
Soft Asphalt, Hub- bard Air-Bath Method	134	135	1
Medium Asphalt, Barrett Mfg. Co. Air-Bath Method	196	197	1
Hydrolene, Barrett Mfg. Co. Air-Bath Method	187	191	4

TABLE II.—COMPARISON OF RING-AND-BALL METHODS.

Method.	Size of Ring (brass).			Size of Attached Wire, in.	Diameter of Ball (steel), in.	Bath. Glycerin for high M. P. water for low M. P.	Size of Beaker.	Amount of Liquid.	Distance of Ring from Bottom, in.	Rate of Heating, per minute.
	Diameter, in.	Depth, in.	Thickness, in.							
Barrett Mfg. Co., Chicago Laboratory	11/16	5/8	1/64	5/32	3/8	Water for low M. P.	600 cc.	400 cc.	1	Water—5° C. Glycerin—7° C.
Barrett Mfg. Co., Philadelphia Lab- oratory	5/8	3/8	1/8		1/4					
Standard Oil Co. and Atlantic Refining Co.	5/8	1/4	3/32	1/16	3/8	Water or Oil.	3 in. diam.	2 in.	1	10° F.
Gulf Refining Co....	5/8	3/8	3/32		1/4	Glycerin	200 cc.	Two- thirds.	1 1/2	5° F.
U. S. Asphalt Refin- ing Co.	5/8	1/4	3/32	Adjustable support	3/8			full		

NOTE.—The melting point in all cases is taken when ball touches bottom of apparatus; the temperature at the start is not given. At the Chicago laboratory of the Barrett Mfg. Co. the liquid is stirred.

TABLE III.—COMPARISON OF MELTING POINTS OF HARD, MEDIUM AND SOFT ASPHALTIC MATERIALS.
All Results in Deg. Fahr. Rate of Temperature Rise in All Cases = 9° F. or 5° C. Per Minute.

Material.	No. 1, 1/2-in. Cube, Cot- tonseed-Oil Method.		No. 2, Hubbard, Air- Bath Method.	No. 3, Barrett Mfg. Co., Air-Bath Method.	Difference between Nos. 1 and 2.	Nos. 2 and 3.	No. 4, Chicago Barrett Mfg. Co., Ring and Ball Method.	No. 5, Standard Oil Co., & Atlantic Rfg. Co., Ring and Ball Method.	Difference between Nos. 4 and 5.	Nos. 4 and 2.	Nos. 2 and 5.	No. 6, Chicago Barrett Mfg. Co., Ring and Ball Method.	No. 7, Standard Oil Co., Ring and Ball Method.	No. 8, 1/2-in. Cube in Water.	Difference between Nos. 6 and 7.
Atlantic Rfg. Co., Philadelphia Asphalt	292	277	262	15	15	280	260	20	3	17					
Atlantic Rfg. Co., Asphalt	263	250	236	13	14	255	235	20	5	15					
Parolite from Standard Oil Co.		250	239		11		225			25					
Hydrolene, Sun Co.		194	187		7		175			19					
Texas Asphalt Co.	246	230	214	16	16	237	212	25	7	18					
Oxidized Flux Oil		160	155		5	181	161	20	21	1	178	160	178		18
"D" Grade Asphalt		144	140		4	158	139	19	14	5	146	131			15
Chicago Mixed Asphalt		124	118		6	133	117	16	9	7	128	113			15
Flux Oil		115	107		8	112	105	7	—3	10	109	97			12
Flux Oil		108	101		7	107	100	7	—1	8	105	94			11

¹Glycerin bath used.

²Water bath used.

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NOTES AND COMMENTS.

Brazilian Carnauba Wax.

The vegetable wax obtained from the leaves of the carnauba palm is used in the manufacture of phonograph records, shoe polish, candles, and other articles, and is an export of some importance from Brazil. U. S. Consul Robert Frazer, Jr., Bahia, Brazil, reports that the shipments from his district and from the whole country for the years 1910, 1911, and 1912, the last for which complete figures are available, were:

Port of export.	1910 Metric tons.	1911 Metric tons.	1912 Metric tons.
Para	0.8	11.4	28.5
Sao Luis, Maranhao.....	114.9	37.4	94.5
Ilha do Cajueiro.....	841.9	886.1	917.9
Camocim			9.0
Fortaleza	678.9	1,253.6	1,238.7
Natal	3.6	21.9	2.5
Pernambuco	858.2	911.4	670.0
Bahia	182.7	89.5	138.0
Rio de Janeiro.....		2.8	
Total	2,681.0	3,214.1	3,099.1

Exports from the Bahia district to the United States alone in the last three years were valued as follows: 1911, \$13,690; 1912, \$16,615; 1913, \$14,501. None was shipped in the first six months of 1914. The last consignments invoiced at this consulate in 1913 were worth \$585 to \$590 per metric ton of 2,204.6 lbs. The wax shipped from Bahia is not produced in this imme-

diate vicinity, but is brought from the interior, chiefly in the neighborhood of the San Francisco River. It is not prepared in large factories, but is worked on a small scale by individuals in the swamp lands where the palm grows, from whom it is then collected by middlemen and sent to the ports for shipment.

War Should Result In Increased American Pottery Exports.

The American demand for several minor mineral products will be stimulated by the changes in trade with Europe, with the result of increasing materially the production for 1914 and following years. In the case of pottery this movement toward a stronger hold of the domestic market is already well under way. The production in 1913 was the largest in the history of the industry. The underlying cause of this prosperity is no doubt the improvement in the character of the American product in texture, finish, color, decoration, and the prevention of crazing, the higher grades of American pottery equaling if not surpassing some of the best imported ware. For many years the value of the imported pottery exceeded the value of that made at home, but about the close of the nineteenth century domestic production caught up with imports, and since that time it has greatly exceeded them.

Resignation of David T. Day.

The report on the production of petroleum in 1913, just issued by the United States Geological Survey, is the last one which will bear the name of David T. Day as author, Dr. Day having resigned from the Survey to engage in private practice. It is expected, however, that he will contribute to next year's report a short chapter on the general petroleum industry. The work of gathering the statistics on petroleum and compiling this Government report has now been placed in full charge of John D. Northrop, a geologist of the Survey who has become familiar with the general trend of the petroleum industry by many years' experience in geologic work in the oil fields of the United States. During the seven years that Dr. Day has been author of this important annual report of the Geological Survey his statistical contributions have recorded an enormous increase of the petroleum industry. In 1907 the output was 166,095,335 bbls. and Oklahoma was the largest producer, with a record of 43,524,128 bbls. In 1913 California was the largest producer, with a record-breaking output of 97,788,525 bbls., and the total for the United States was 248,466,230 bbls.

Platinum Mining Difficulties.

Although the high price of platinum encouraged prospecting in the United States during 1913, the expected increase in the production of crude metal was not realized. The total production from California and Oregon, according to the United States Geological Survey, amounted to 482.87 crude ounces and was valued at \$18,477. Of this, 460.37 crude ounces came

from California and were rated at 80 per cent fine—that is, it contained 368.3 fine ounces of platinum. That from Oregon—22.5 ounces—was not so carefully cleaned and was reckoned at 70 per cent fine, or 15.75 fine ounces of platinum. The greater part of the California platinum came, as usual, from the large gold-dredging operations in Butte, Yuba, Sacramento, and Calaveras Counties. The production of refined platinum in the United States from domestic sources in 1913 was 1,034 troy ounces, valued at \$46,530. The question of a larger yield of domestic platinum depends principally upon working the Oregon and California beaches, including the old beaches now several miles inland and elevated considerably above sea level. Several machines involving somewhat fanciful or novel ideas were installed during 1913. As a rule, these machines were handicapped because they consisted either of competent concentrating apparatus without adequate means for digging the crude sand and delivering it to the concentrator, or, in other places, the reverse has been the case, and the machine, well suited for large-scale excavation at a low cost, has not been equipped with a proper system for concentrating these heavy sands after excavating them. The platinum industry remains practically stationary with reference to the world's supply and the price. The supply from the well-known placers of Russia continues to decline slowly, but the uses for platinum do not increase sufficiently to cause the price to advance on account of the decline in supply. If more platinum were greatly needed, the supply could be augmented from California and Oregon.

The Annual Meeting of the American Institute of Chemical Engineers.

The Seventh Annual Meeting of the American Institute of Chemical Engineers will be held in Philadelphia, Pa., Dec. 2-5. A program of excursions to a number of the large chemical manufacturing plants in and around Philadelphia is being arranged for. A number of addresses and papers on "The Present Opportunities for American Chemical Industries" will be delivered by prominent chemical engineers and business men. The papers to be presented are as follows:

"The Manufacture and Application of the Artificial Zeolites (Permutite) in Water Softening." (Illustrated with lantern slides, samples of the products, etc.) D. D. Jackson.

"Feldspar as a Possible Source of American Potash." Dr. Allerton S. Cushman, director of the Institute of Industrial Research, and Dr. Geo. W. Coggeshall.

Address: "Distribution of Industrial Opportunities." Geo. O. Smith, director of the United States Geological Survey.

"Hydrometallurgical Apparatus and Its Use in Chemical Engineering." John V. N. Dorr.

"Hardwood Distillation Industry." Illustrated with lantern slides. E. H. French and James R. Withrow.

"Chemical Industries of Japan." Illustrated with lantern slides. Jokichi Takamine.

"Need of Up-to-date Manufacturing Statistics." Barnard C. Hesse.

"Ore Flotation, a New Hydrometallurgical Development." Illustrated by demonstrations of working models. Froths will be made with several kinds of ore and several different agents. Dr. S. P. Sadtler and S. S. Sadtler.

"Aspects of Some Chemical Industries in the United States Today." Dr. Edw. Gudeman.

Synthetic Ammonia.

Readers of *The American Fertilizer* are familiar with the various descriptions we have published of the Haber process for the production of ammonia from its elements by subjecting the gases—nitrogen and hydrogen—to an enormous heat under a pressure unusually heavy for commercial purposes. The combination was effected by the aid of a metallic catalytic agent. Professor Haber's standing in the world of science is well established, and the announcement that he had successfully accomplished the manufacture of ammonia in such a manner even on an experimental basis was received with a vast amount of interest by those interested in the fields consuming ammonia in a large way. When the further announcement was made that the Badische Anilin and Sodafabrik of Ludwigshafen, reputed to be the largest chemical manufacturing concern in the world, had taken up the process and proposed financing it, the scientific world was convinced at once that the laboratory had again produced a process that gave promise of tremendous commercial possibilities.

In January of the current year the Badische Company and the Bayer Company, another gigantic German chemical manufacturing enterprise, entered into an agreement whereby the process as devised by Professor Haber was to be developed under their joint control. Since then the Badische Company has increased its capital from \$9,000,000 to \$12,500,000, and the Bayer Company has increased its capital from \$9,000,000 to \$13,500,000. These increases are to finance the developments of the manufacture of synthetic ammonia, a plant for the manufacture of which is now being erected at Oppau by the Badische Company. The increase in the capitalization of the two companies is about 44 per cent, and reveals at a glance that the German chemists have an abundance of faith in the process.

We believe it is therefore quite safe to assume that during the course of the next few years sulphate of ammonia and other ammonium salts produced direct from nitrogen and hydrogen will make their appearance on the market. The world's consumption of ammonia in various forms is now many million tons annually, and the production of nitrogen carrying chemical salts has been increasing at an extensive rate the past few decades.—*American Fertilizer*.

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HYDROGEN, ITS TECHNICAL PRODUCTION AND USES.

By A. F. SEEKER.*

In recent years the cheap production of hydrogen on a large scale for technical purposes has become a problem of some importance. Formerly it was used occasionally for filling balloons and in the oxy-hydrogen flame of the so-called "calcium light." Being the lightest of the common gases and of a correspondingly high sustaining power, it has become essential for the filling of dirigible balloons with their heavy burden of propelling machinery. Such uses, however, have become of rather secondary importance, and it will probably be only a short time before the dirigible balloon and the "calcium light" will have been permanently discarded in favor of heavier than air machines and the varied forms of projected lights operated by electricity.

The oxy-hydrogen flame is now becoming a common tool in the hands of the artisan in working refractory metals; liquid oils and soft greases are now "hydrogenated" to produce acceptable lard and butter substitutes, and also solid fat suitable for the manufacture of hard soaps; and lastly, the use which promises to consume enormous quantities, ammonia is manufactured from hydrogen and atmospheric nitrogen. All these uses tend to make the problem of the production of cheap hydrogen one of considerable importance.

The employment of the oxy-hydrogen torch is too well known to require description here. The commercial "hydrogenation" of oils and fats is of recent introduction. The process consists in treating the oil or grease in a suitable vessel containing a catalysing agent, generally nickel, with hydrogen under pressure. The oil is violently agitated in order to bring it into intimate contact with the hydrogen and catalyser. The result is that the glycerol esters, of the unsaturated fatty acids, which generally consist for the most part of oleic acid, become saturated, and the mono-, di-, or triolein, as the case may be, is converted into the corresponding stearin. The oleins are either liquid or semi-solid at ordinary temperature, and produce soft soap or soap that will not hold much water without becoming soft. The stearins are solid fats at ordinary

temperatures and produce hard soaps. Thus by the process of hydrogenation, cotton seed and corn oils are today being converted into lard and butter substitutes, and the soft waste grease which formerly could only be used sparingly in soap on account of their softening effect can now be employed alone as soap stock. The importance of this is understood when the constantly soaring prices of animal tallow are taken into consideration.

In view of the impending exhaustion of the Chili nitre beds, the problem of the fixation of atmospheric nitrogen for the manufacture of artificial fertilizers has received constantly increased attention. Electrical methods for the production of cyanimid from calcium carbide and nitrogen, and the flaming arc process for making nitric acid directly from the air have been established upon a successful commercial footing, but these require such an enormous expenditure of energy that they can only be operated profitably where there is an abundance of cheap water power. If only these processes were available, countries lacking in water power would be placed at a distinct disadvantage, and for this reason many chemists, particularly those of Germany, have labored to find a process better suited to the conditions surrounding them. The details of this search were described in a most interesting manner before the Eighth International Congress of Applied Chemistry, by Hofrat Dr. H. A. Bernthsen, who is the Chemical Director of the Badische Anilin and Soda Fabrik, the owners of a synthetic ammonia factory now in successful operation at Oppau, near Ludwigshafen on the Rhine.

The process, which has been named after Haber, its inventor, consists in passing a mixture of pure nitrogen and hydrogen under a pressure of 150 to 250 atmospheres through a tube filled with a catalyzer and heated to 650 to 700° C. The hot gases then pass through a heat regenerator and thence through an ammonia absorber, after which they are replenished with fresh gas mixture and forced by a pump back over the outer walls of the contact tube and then through the contact mass to repeat the circulatory course already described. Only a part of the gas mixture is converted into ammonia by a single passage through the converter, but the gases are made to circulate continuously through the apparatus, the ammonia being absorbed each time as the mixture issues

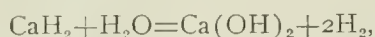
*Polytechnic Engineer.

from the heat regenerator at the end of the contact tube. The gases are replenished with fresh hydrogen-nitrogen mixture as required. The contact mass consists of pure iron containing small amounts of certain so-called promoters which may consist of oxides, hydroxides, or salts of the alkalies or of the alkaline earths, and also many other substances of the most varied nature, especially metallic compounds or the metals themselves.

There have been many ways proposed for the producing of hydrogen on a large scale the most important of which are the electrolytic and the water gas process. The studies of A. Wegener and others lead to the belief that at an altitude of about 75 miles the atmosphere consists of pure hydrogen and nitrogen that would be ideal for the Haber process. Unfortunately no means of piping these gases down to our sphere of action are known and we must content ourselves with more laborious methods of production.

At European army posts, hydrogen for military balloons is commonly generated from scrap iron and sulphuric acid, the reaction being accelerated by heating the mixture to about 55° C. For field operations zinc is used in place of iron and the generators are mounted on wheels to facilitate transportation. Three other, and more modern means, of generating hydrogen are used for field purposes and will no doubt be adapted for other than military uses in places difficult of access where the gas is needed. These processes were invented by G. F. Jaubert, a Frenchman, and were named by him respectively, the "Hydrolith," "Silicol," and "Hydrogenite" processes.

Hydrolith is formed by heating metallized calcium in an atmosphere of hydrogen, producing a hydride, CaH_2 , which when treated with water reacts as follows:



just as calcium carbide generated acetylene. Hydrolith is a white crystalline powder, decomposing at 600 degrees in a vacuum, and usually contains about 90% of CaH_2 , the rest being nitride and oxide. One kilogram yields about one cubic meter of hydrogen. The apparatus designed for using hydrolith in the French army is very ingenious, can readily be transported and has a capacity of 1,200 cubic meters per hour. An army dirigible can be filled in four hours. The high cost of Hydrolith, \$1.33 per kilogram, will at present seriously restrict its use outside of military operations.

The Silicol process consists in treating powdered ferrosilicon, or mangano-silicon with water and caustic soda. It does not appear to have gained extended use because of the more troublesome manipulations and the greater difficulty of controlling the evolution of gas as compared with the other methods.

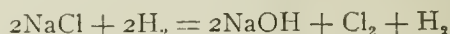
Hydrogenite is composed of ferrosilicon, (containing 90 to 95 per cent of metallic silicon) 25 parts, caustic soda 60 parts and dry slaked lime 20 parts. The ingredients are reduced to a very fine powder, intimately

mixed, and pressed into brick weighing 25 to 50 kilograms. Being very hygroscopic, each brick must be sealed in a tin box to prevent decomposition. In generating hydrogen the brick is placed in a metal chamber having double walls, the space between the two walls being filled with water. Vents are placed in the upper part of the inner wall leading to the central chamber containing the Hydrogenite so that the steam formed during the combustion may gain access to the charge and increase the yield. The cover of the tin containing the Hydrogenite is opened, the tightly fitting lid of the generator fastened in place and through a small hole in the latter a red hot wire is thrust into the charge. The mass burns quickly, without flame, generating heat and evolving hydrogen according to the equation:

$\text{Si} + \text{Ca}(\text{OH})_2 + 2\text{NaOH} = \text{Na}_2\text{SiO}_3 + \text{CaO} + 2\text{H}_2$;
One volume of the compressed Hydrogenite yields 800 volume, or 270 to 370 liters per kilogram, of pure hydrogen, at a cost of about 32 cents per cubic meter. The requisite apparatus for field purposes weighs about 900 kilograms.

The methods employed upon a large scale are, of course, capable of producing the gas much more cheaply. In one of these an iron, clay lined retort is filled seven-eighths full of coke, ignited and raised to a white heat by an air-blast. The retort is then closed and a cheap hydrocarbon like crude petroleum or coal tar is injected into it from the top for about 20 minutes or until the temperature has fallen below the proper cracking point, the gas thus generated passing through a sprinkling tower and filtered into the gasometer. The oil injector is then shut off, the retort opened, the air blast again turned on, and the process repeated indefinitely with periodical renewal of the coke and removal of the ashes. The product contains about 2.7 per cent CO, 96.0 per cent H, and 1.3 per cent N, and has a specific gravity of 0.1. The gas can be still further purified to a content of 98.4 per cent H, by passing it through suitable absorbents, and is produced at a total cost of 3 to 4 cents per cubic meter, according to the size of the plant and the materials used.

Large amounts of hydrogen are obtained as a by-product in the electrolysis of salt solutions in the manufacture of chlorine and of caustic soda. The electrolysis is effected in a cell having a cement diaphragm which is not attacked by chlorine or caustic soda. The electrodes are iron and carbon, the latter being used as an anode. The reaction which is as follows:



yields 7,000 cubic feet of hydrogen for every ton of salt. A cell operates on 15,000 horsepower at Griesheim, Germany, producing 245 million cubic feet of hydrogen per annum.

To other methods, now little used, consist, (1) in passing superheated steam over red hot iron, and (2) in conducting water gas through suitable absorbents so that the carbon-monoxide and hydro-carbons are

removed, leaving behind the hydrogen and nitrogen. A third process which is increasing in application was devised by Linde, Frank and Caro. In this, water gas which consists mainly of carbon monoxide and hydrogen is compressed and cooled to the liquefying point of the carbon monoxide. Upon relieving the pressure the mixture expands and in so doing is cooled still further so that the carbon monoxide and most of the impurities separate out in liquid form, allowing the hydrogen to pass off in a fairly clean (97 to 98 per cent H) condition. The mixture containing the liquid carbon monoxide is later vaporized and used in combustion motors for power.

The growing demand for cheap hydrogen for industrial uses will act to promote improvements in both the electrolytic and the water gas processes because both require comparatively cheap raw material. The former will probably be favored in districts having abundant water power, whereas the latter requires cheap coal as an initial factor. In any event the extensive growth of the field of application will furnish sufficient incentive for the determination of still more economical processes than now exist.

WOLFRAM MINING IN SIAM.

Vice Consul General Carl C. Hansen, Bangkok, reports that mining for wolfram in Siam is of recent development. According to a report published in the Directory for Bangkok and Siam, this mineral had been known to the Chinese tin miners for a long time as "dead ore," but its commercial value was unknown until some of the ore was taken to Singapore for analysis, and this black mineral was found to be wolfram and to have a workable value.

The richest deposits of wolfram were found in Nakon Sri Tamarat on the east coast of the Siamese portion of the Malay Peninsula. Here the wolfram ore had been left in great heaps as valueless material after having been separated from the tin ore by the Chinese miners. The amount of wolfram recovered during the fiscal year 1912-13 was 309 tons, against 119 tons for the previous year. It is said, however, that the output of this ore is likely to diminish soon, as the surface workings are now nearly exhausted, and that for the working of the deeper deposits on proper lines special knowledge and considerable capital will be needed.

Not long ago a European company started working for wolfram in Koh Samui, an island near Nakon Sri Tamarat, but the experiment was not successful and the works have now been abandoned. Wolfram in moderate quantities has also been found at Puket on the west coast of the Siamese Malay Peninsula, and this mineral is said to be fairly widely distributed throughout the peninsula.

THE SEPARATION OF THE ILLUMINANTS IN MIXED COAL AND WATER GAS.*

By G. A. BURRELL and I. W. ROBERTSON.†

INTRODUCTION.

In this paper are shown experiments made by the Bureau of Mines that resulted in separating the illuminants in the artificial gas of Pittsburgh. This gas is made by mixing 1 part of carburetted water gas with 3 parts of coal gas. The separation was made by fractionally distilling the gas in a vacuum at low temperatures, and follows the method detailed by the Bureau in separating natural gases.¹

In both the natural-gas work and the coal-gas work advantage was taken of work on the subject by P. Lebeau and A. Damiens², who separated mixtures of the paraffin hydrocarbons and coal gas by the same method. The Bureau, however, separated the paraffin hydrocarbons into single constituents and found it necessary to refractionate distillates and residues in all cases to obtain pure gases. Lebeau and Damiens make no mention of this latter necessity and separated the paraffins in pairs. Further, there is shown in this paper a simple method for the determination of benzene in artificial gas. The principle of the procedure rests on the fact that the gases at different stages in the analysis are subjected to temperatures at which certain constituents can be removed by a mercury pump from certain others which have low vapor tensions at the temperature selected. It was found impossible to make a clean separation in any case at one fractionation, hence distillates and residues were refractionated until the separation was as complete as was desired.

The following groups show the constituents of artificial gas that can be separated at different temperatures. The first column shows the distillates that can be obtained at a particular temperature and the second column the residues, i. e., those gases that have inappreciable vapor pressures at the temperatures given.

Temperature of Liquid Air.

Distillate—	Boiling point. Deg. C.	Residue—	Boiling point. Deg. C.
Methane (CH ₄)	—160	Ethane (C ₂ H ₆)	—93
Nitrogen (N ₂)	—195	Propane (C ₃ H ₈)	—45
Oxygen (O ₂)	—183	N-butane (C ₄ H ₁₀)	1
Carbon monoxide (CO)	—193	Iso-butane (C ₄ H ₁₀)	10
Hydrogen (H ₂)	—253	Ethylene (C ₂ H ₄)	—103
		Propylene (C ₃ H ₆)	—51
		Iso-butylene (C ₄ H ₈)	4
		Benzene (C ₆ H ₆)	80

*Presented at the meeting of the American Gas Institute, New York City, Oct. 20, 1914, with the permission of the Director of the Bureau of Mines.

†United States Bureau of Mines.

¹Burrell, G. A., and Selbert, F. M., Gas analysis by fractional distillation at low temperatures. Jour. Amer. Chem. Soc., vol. 36, No. 7, July, 1914, pp. 1538-1548.

²Comptes rendus, vol. 156, p. 325, 1913; vol. 156, p. 797, 1913.

³The boiling point of N-butylene could not be found in the literature. The N-butylene was not separated from the iso-butylene. Neither was the N-butane separated from the iso-butane.

-155° C. to -145° C.			
Distillates—	Boiling point, Deg. C.	Residue—	Boiling point, Deg. C.
Ethylene (C ₂ H ₄)	-103	Propane (C ₃ H ₈)	-45
Ethane (C ₂ H ₆)	-93	N-butane (C ₄ H ₁₀)	1
		Iso-butane (C ₄ H ₁₀)	-10
		Propylene (C ₃ H ₆)	-51
		Iso-butylene (C ₄ H ₈)	-4
		Benzene (C ₆ H ₆)	80
-130° C. to -120° C.			
Propane (C ₃ H ₈)	-45	N-butane (C ₄ H ₁₀)	1
Propylene (C ₃ H ₆)	-51	Iso-butane (C ₄ H ₁₀)	-10
		Iso-butylene (C ₄ H ₈)	-4
		Benzene (C ₆ H ₆)	80
-78° C.			
N-butane (C ₄ H ₁₀)	1	Benzene (C ₆ H ₆)	80
Iso-butane (C ₄ H ₁₀)	-10		
Iso-butylene (C ₄ H ₈)	-4		

COMPOSITION OF THE ARTIFICIAL GAS OF PITTSBURGH AS ANALYZED BY ORDINARY METHODS.

Analysis made Sept. 1, 1914.

Constituents.	Per Cent.
Carbon dioxide (CO ₂)	2.64
Oxygen (O ₂)	.81
Illuminants	8.67
Carbon monoxide (CO)	13.34
Hydrogen (H ₂)	37.04
Methane (CH ₄)	30.96
Ethane (C ₂ H ₆)	1.82
Nitrogen (N ₂)	4.72
Total	100.00

In making the above analysis the carbon dioxide was removed by the caustic-potash solution, the oxygen by alkaline pyrogallate solution, the illuminants by fuming sulphuric acid, the hydrogen by absorption in colloidal-palladium⁴ solution, the methane and ethane by slow combustion, and the nitrogen by difference.

The above gas was next subjected to fractional distillation at various low temperatures in the apparatus shown in Fig. 1 (apparatus for the liquefaction and fractionalation of gases). At *a* is shown a Dewar flask to hold the refrigerant used in cooling the gases. *b* is the bulb in which the gases were cooled. *d* is a gas-analysis burette and *c* another gas container for measuring the gases prior to cooling. *e* is a pressure gage for registering pressures in the Töpler pump. *f* is a drying tube containing phosphorus pentoxide for removing the water vapor from the gases. *g*, *h* and *i* are containers for trapping the gases over mercury as they were removed from the pump. *h* and *i* are provided with 3-way stopcocks. The particular advantage of containers such as are shown at *h* and *i* lies in the fact that they could be filled with mercury by forcing down on them with the stopcock open to the air, finally filling the capillary tubes with mercury. The gas from the pump could then be introduced into them by means of the goose-neck tube attached to *l*, leaving a mercury seal in the capillary tube all the time. *j* is a pressure gage which was of principal use in the benzene determination. *o*, *n* and *m* are 3-way stopcocks. A counterpoise *p* attached to the mercury reservoir of the Töpler pump greatly facilitated the working of the pump.

FIRST SERIES OF FRACTIONATIONS.

In Fig. 2 are shown the various steps in the main separation of the gas.

The original volume of sample (2,048 cc.) was first freed of the carbon dioxide by passing it through caustic-potash solution; 53 cc. of carbon dioxide was removed, leaving 1,995 cc. The latter quantity of gas was then cooled in the bulb *b* (Fig. 1) (about 300 cc. at a time), at the temperature of liquid air. After the introduction of each 300 cc., pumping was started and as much of the gas removed as possible. There re-

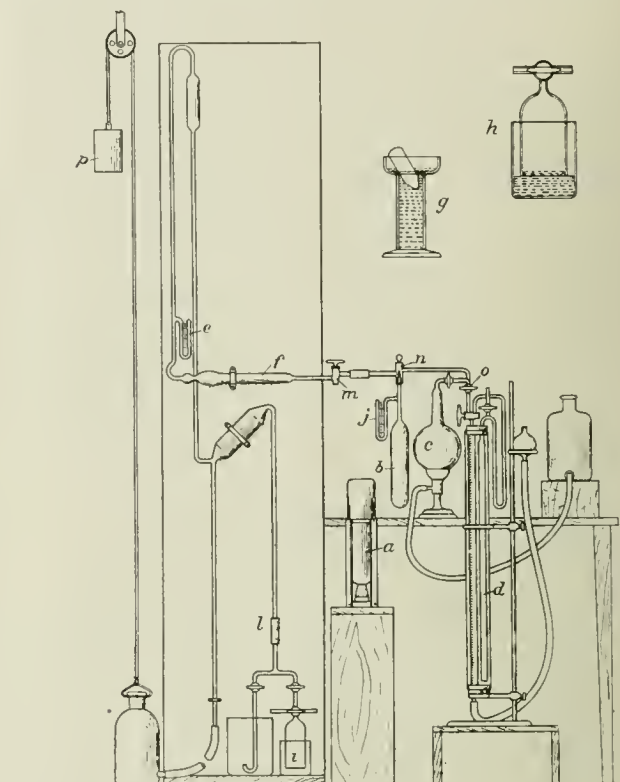


Fig. 1.

sulted a distillate (*a*) and a residue (*b*). The distillate (*a*) was fractionated at the temperature of liquid air, resulting in two more fractions (*c*) and (*d*). (*d*) was added to the residue (*b*) and the total again fractionated at the temperature of liquid air. The distillate (*f*) thus obtained was added to the distillate (*c*) and the total again fractionated at the temperature of liquid air. The residue thus obtained (10 cc.) was added to the residue (*e*) and the total again fractionated. There resulted a distillate (*g*) of 3 cc. which was added to the distillate (*i*) making a total of 1,782 cc. This first series of fractionations shows the general procedure. At the temperature adopted, in this case the temperature of liquid air, the gases were repeatedly fractionated until no more distillate of consequence could be obtained. 3cc., the final distillate obtained, is only about 0.15 per cent of the original quantity of gas (2,048 cc.) taken for the experiment. The total distillate obtained at the temperature of liquid air was 1,782 cc., and consisted of those gases that have an appreciable vapor tension at that temperature. This fraction consisted of .81 per cent of oxygen, 13.25 per cent of carbon monoxide, 37.33 per cent of hydrogen, 31.13 per cent of methane, and 4.23 per

⁴See Burrell, G. A., and Oberfell, G. G., The absorption of hydrogen by colloidal-palladium solution. Jour. Ind. Eng. Chem., vol. 6, No. 8, Nov., 1914.

cent of nitrogen. It will be observed that the quantities of these constituents check very well with the quantities of the same constituents found in the original ordinary analysis of the coal gas. The residue of the first series of fractionations (191.6 cc.) should consist of those gases and vapors that do not have an appreciable vapor pressure at the temperature of liquid air. They are C_2H_6 , C_3H_8 , C_4H_{10} , C_2H_4 , C_3H_6 , C_4H_8 , and C_8H_8 . In other words, the so-called illuminants of coal gas with the addition of ethane and probably propane.

SECOND SERIES OF FRACTIONATIONS.

The residue (h) (191.6 cc.) was next cooled at temperatures ranging from -155° C. to -145° C. and as much gas removed as possible with the mercury pump. Distillates and residues were repeatedly fractionated until there was obtained 167.0 cc. of gas consisting of ethane and ethylene. This fraction was analyzed in two ways, first by burning the entire fraction with oxygen and (2) by first removing the ethylene with fuming sulphuric acid and then burning the ethane in oxygen. The data covering these two methods of analysis follows:

ANALYSIS OF ETHANE AND ETHYLENE.
ANALYSIS BY COMBUSTION.

	Cc.	Per Cent.
Sample taken	15.12	
Oxygen added	94.42	
Total volume	109.54	
Volume after burning	78.00	
Contraction produced	31.54	
Volume after KOH absorption.....	48.27	
Carbon dioxide produced	29.73	
Ethane		23.90
Ethylene		74.40

ANALYSIS BY ABSORPTION AND COMBUSTION.

Sample taken	34.18
After absorption in fuming H_2SO_4	8.85
Absorbed by fuming H_2SO_4	25.33
Oxygen added	76.28
Total volume for combustion	85.13
Volume after burning	64.95
Contraction	20.18
Volume after KOH absorption	49.02
Carbon dioxide produced by burning ..	15.93
Ethane	
Ethylene	

It will be observed that the ethane and ethylene as found by the two methods of analysis check very well, showing that other gases were not present in the distillate in significant amounts. The percentages as found above were averaged and calculated to percentages of the original coal gas.

THIRD SERIES OF FRACTIONATIONS.

After the removal of the ethane and ethylene, there remained 24.4 cc. of gas which was fractionated at temperatures ranging from -130° C. to -120° C. The distillate, 21.1 cc., was analyzed by burning it in oxygen, and measuring the resulting contraction and carbon dioxide and calculating to propane and propylene. This method does not isolate the gases and hence does not show that other gases than these two were not present. In working on the separation of the paraffin hydrocarbons, however, the Bureau found that propane could be separated from ethane at temperatures

between -130° C. and -120° C. Propylene has a boiling point very close to propane, and the boiling point of ethylene is not far different from that of ethane, hence it is assumed that propylene and ethylene would respond to the same treatment as the propane and ethane.

FOURTH SERIES OF FRACTIONATIONS.

After removing the propylene and propane, there remained a residue of 2.3 cc., only 0.11 per cent of the original quantity of gas (2,048.0 cc.). This residue was analyzed by burning it in oxygen, and the

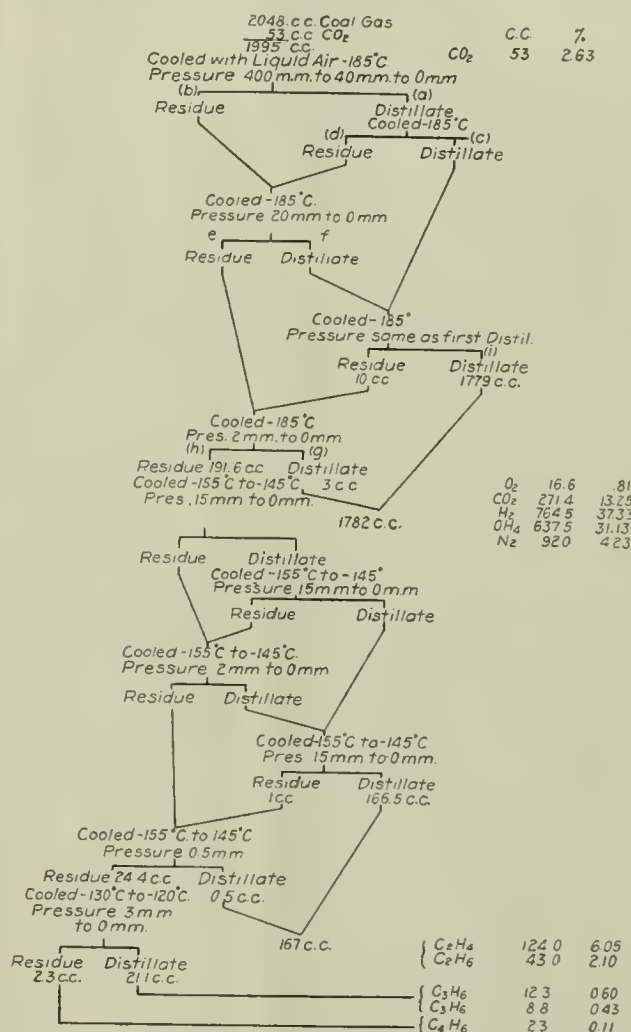


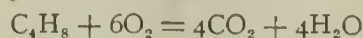
Fig. 2.

contraction and carbon dioxide calculated to butylene. The observed data follow:

ANALYSIS OF BUTYLENE RESIDUE.

	Cc.
Volume taken for analysis	2.3
Oxygen added	93.81
Total volume	96.11
Volume after burning	90.53
Contraction produced	5.58
Volume after KOH absorption	82.86
Carbon dioxide produced by burning	7.67

According to the reaction



there result 3 volumes contraction and 4 volumes carbon dioxide, when butylene reacts with oxygen. The

contraction and carbon dioxide observed in the above analysis, 5.58 cc. and 7.67 cc., are almost in the ratio of 3:4, within the error of making the analysis, hence the data were calculated to butylene. Such a small quantity of gas was available to work upon that there might easily have been a trace of butane present. However, the total quantity compared to the original volume was only 0.11 per cent, or practically insignificant. Benzene that should have appeared in this last fraction did not show up, hence it was inferred that, in the many transfers of gas, it had remained in the pump and removed, a trace at a time, in the other fractions and in sweeping out the pump with air.

The total number of cubic centimeters of gas from the various fractions equals $1,782 + 167 + 21.1 + 2.3 = 1,972.4$ cc. This is exclusive of the benzene. The benzene as found by using a separate portion of the coal gas is 1.33 per cent of the coal gas. Then $2,048$ cc. $\times 1.33$ per cent = 27.2 cc., and $1,972.4$ cc. + 27.2 cc. = $1,999.6$ cc., or within about 5.0 cc. of the amount (1,995 cc.) that was fractionated. Considering the number of times the different fractions of gas were handled and measured in the fractionation analysis, this is not a bad check on the operation.

DETERMINATION OF BENZENE.

For the benzene determination a separate quantity of coal gas was used, and advantage taken of an apparatus suggested by Dr. G. A. Hulett, Chief Chemist of the Bureau, for the determination of water vapor in air. Dr. Hulett suggested that air with its moisture be cooled at the temperature of liquid carbon dioxide and the air be then removed with a mercury pump, and the water vapor be determined after removing the cooling medium, by measuring its pressure. It was a simple matter to apply this principle to the determination of benzene in coal gas. The procedure was to free the coal gas of carbon dioxide and water vapor and introduce it into the liquefaction bulb (b) (Fig. I), cool it at a temperature of -78° C. and remove as much gas with the pump as possible. The stopcock (n) on the bulb was then closed and the Dewar flask containing the cooling medium removed. The condensed liquid in the bulb was then vaporized and its pressure read on the manometer (j) (Fig. I). This pressure compared to the original pressure of the gas gave the percentage of benzene in the coal gas. The results of two determinations are shown in Table I.

The total illuminants in the coal gas of Pittsburgh as found by absorption in fuming sulphuric acid is 8.67 per cent. The distillate from the benzene determination was analyzed by absorbing the remaining illuminants in fuming sulphuric acid. There was removed 7.32 and 7.39 per cent of the distillates. These amounts when added to the benzene found, 1.31 and 1.34 per cent, equal 8.66 and 8.70 per cent or almost identical amounts with those of the total illum-

inants in the coal gas. Benzene reacts with oxygen as follows:



The contraction is 2.5 volumes and the carbon dioxide is 6 volumes. The following data show the results of analysis of the residual vapor that was held in the liquefaction bulb (Fig. I) when the coal gas was cooled at a temperature of -78° C. Before analysis the benzene vapor was diluted with air.

ANALYSIS OF BENZENE VAPOR.

	Cc.
Volume taken for analysis.....	28.29
Oxygen added	51.94
Total volume	80.23
Volume after burning	75.47
Contraction due to burning	4.76
Volume after KOH absorption.....	64.25
Carbon dioxide produced by burning.....	11.42

It will be observed that the ratio between the carbon dioxide and contraction is almost exactly 6:2.5, showing that the vapor obtained in the determination was benzene. Traces of other easily condensable vapors may have been present but apparently in such small quantity as to be negligible. The authors of this publication were unable to find the vapor pressure of benzene at -78° C. but apparently it is very small. Benzene boils at 80° C. At -20° C. the tension is 5.76 mm.⁵ The authors prepared saturated vapors of benzene by shaking pure benzene with dry air. It was a simple matter to prepare unsaturated vapors of benzene by simply diluting the saturated vapors with air.

The quantity of benzene in the air was found by combustion analysis. A number of tests were made of the benzene in air by the method just described. It was found that at -78° C. all of the benzene could be separated from the air. Analyses were made of the distillates and residues to make sure that all of the benzene remained in the liquefaction bulb at the temperature of -60° C. The foregoing method therefore seems to be well adapted for the benzene determination. There is needed a mercury pump, a liquefaction bulb, a gas burette for introducing the gases, and a Dewar flask for holding the refrigerant. A temperature of -78° C. can easily be obtained by using the liquid carbonic acid sold in tanks. The coal gas does not even have to be measured and its exact volume

TABLE I.—RESULTS OF THE BENZENE DETERMINATION.

Original Pressure of the Gas, Mm. of Mercury.	Partial Pressure of the Benzene Vapor, Mm. of Mercury.	Illuminants Found in the Distillate, Percentage of the Total Coal Gas.	Calculation of Benzene.	Percentage of Benzene in the Coal Gas of Pittsburgh.
744	10	7.32	$\frac{10 \times 100}{744}$	1.34
744	9	7.39	$\frac{9 \times 100}{744}$	1.31

⁵Landolt and Börnstein, *Physikalisch-chemische Tabellen*, 1905, p. 143 (according to Regnault).

determined. It is sufficient to introduce it into the liquefaction bulb at atmospheric pressure and then to read the barometer.

COMPLETE ANALYSIS OF THE ARTIFICIAL GAS OF PITTSBURGH.

The complete analysis of the coal gas as found by the foregoing methods follows:

COMPLETE ANALYSIS OF ARTIFICIAL GAS.		
Constituent.	Formula.	Per Cent.
Carbon dioxide	CO ₂	2.63
Oxygen	O ₂	.81
Carbon monoxide	CO	13.25
Hydrogen	H ₂	37.33
Methane	CH ₄	31.13
Ethane	C ₂ H ₆	2.10
Propane	C ₃ H ₈	.43
Ethylene	C ₂ H ₄	6.05
Propylene	C ₃ H ₆	.60
Butylene	C ₄ H ₈	.11
Benzene	C ₆ H ₆	1.33
Nitrogen	N ₂	4.23
		100.00

ANALYSIS OF A DIFFERENT SAMPLE OF COAL GAS.

There is shown below the analysis of a sample of the coal gas of Pittsburgh collected at a different date than the one already given. It is interesting as showing the marked uniformity of the gas as collected on two days about seven weeks apart. The benzene was not determined in this analysis because the method had not been perfected.

ANALYSIS OF A SAMPLE OF COAL GAS OF PITTSBURGH MADE ON JULY 10, 1914.

Constituent.	Formula.	Per Cent.
Carbon dioxide	CO ₂	2.40
Oxygen	O ₂	.61
Carbon monoxide	CO	13.63
Hydrogen	H ₂	37.13
Methane	CH ₄	30.92
Ethane	C ₂ H ₆	1.92
Propane	C ₃ H ₈	.32
Ethylene	C ₂ H ₄	6.36
Propylene	C ₃ H ₆	.70
Butylene	C ₄ H ₈	.12

HEATING VALUE OF THE ILLUMINANTS IN THE COAL GAS OF PITTSBURGH.

In calculating the heating value of artificial gas from the analysis as ordinarily made, a value is usually assigned to the illuminants that is an approximation because the constituents that make up the illuminants have not been exactly known. With these data at hand for the coal gas of Pittsburgh the authors show below a value calculated from the complete analysis.

TABLE SHOWING THE HEATING VALUE OF THE ILLUMINANTS IN ARTIFICIAL GAS.

Constituents.	B. t. u. per cubic foot at 0° C. and 760 mm. pressure.*	Constituents present in the coal gas.	Heating value of the constituents present in the coal gas.
Ethylene	1,673	.0605	101.21
Propylene	2,509	.0060	15.05
Butylene	3,265	.0011	3.59
Benzene	4,012	.0133	53.36
Propane	2,654	.0035	9.29
		0.844	182.50

*These heating values were calculated from the values as found by Thomsen. His values are given in Landolt and Börnstein's Physikisch-chemische Tabellen, 1905, p. 425. They are given in large calories per gram-molecule.

According to the above calculations the so-called illuminants in coal gas have a heating value at 0° C. and

$$182.50 \times 100 \\ 760 \text{ mm. pressure of } \frac{\quad}{8.44} = 2,162 \text{ B. t. u.}$$

The authors have included propane in the illuminants as ordinarily determined by absorption in fuming sulphuric acid because propane dissolves to a certain extent in the acid. Just how much is not known. It was found that the methane and ethane⁷ were soluble to a slight extent. Unquestionably propane is much more so because the higher paraffins are more soluble than the lower ones. Excluding propane the heating value

$$173.2 \times 100 \\ \text{of the illuminants becomes } \frac{\quad}{8.09} = 2,141 \text{ B. t. u.}$$

per cubic foot at 0° C. and 760 mm. pressure.

ADDITIONAL DETAILS OF THE EXPERIMENT.

Temperatures higher than the temperature of liquid air were obtained by cooling a natural-gas condensate. This condensate was obtained from a natural-gas gasoline plant by subjecting natural gas (casing-head gas) from an oil well to a pressure of 250 pounds per square inch and then cooling it to ordinary temperatures. A steel cylinder such as is used in transporting oxygen was shipped to the natural-gas gasoline plant of the Bessemer Gas Engine Company at Follansbee, West Virginia, for the purpose of collecting the condensate. This condensate is known in the natural-gas gasoline trade as "wild" gasoline. It contains large quantities of liquid propane and the butanes, especially the latter, as well as some of the ordinary gasoline constituents—the pentanes, hexanes, etc. Ordinary refinery gasoline, and other substances such as alcohol, ether, methyl and ethyl chloride, jellied so much at low temperatures that they could not be used satisfactorily. In order to obtain a temperature higher than the temperature of liquid air, say —145° C., the condensate was placed in a Dewar flask and stirred with a test tube into which liquid air was run until —145° C. was reached. Upon removal of the test tube containing the liquid air the condensate warmed up slowly, about 5° C. to 10° C. per hour, thereby affording sufficient time for the withdrawal of the vapors. If the condensate rose to a higher temperature than was desired, it was a simple matter to introduce a little more liquid air and cool it.

Temperature measurements were made with two pentane thermometers. They agreed with each other and gave within 1.5° C. the true melting points of chloroform and carbon disulphide, and the sublimation point of liquid carbon dioxide. Fresh liquid air as it usually reached the laboratory from a plant near-by had a temperature of —193° C.

The determination of hydrogen sulphide, acetylene, carbon disulphide, ammonia, etc., that might have been

⁷See Burrell, G. A., and Seibert, F. M., The sampling and examination of mine and natural gases. Bulletin 42, U. S. Bureau of Mines, p. 47.

present in the gas was not attempted, because the method used is scarcely adapted to the estimation of the traces of these constituents that are present in coal gas.

Future work on the fractionation of artificial illuminating gas will cover the analyses of gas that is used in other cities than Pittsburgh and the separation of the illuminants in the coal gas before it is mixed with carburetted water gas and in oil gas that is used to enrich water gas.

IMPROVING THE COPRA INDUSTRY IN PHILIPPINES.

An effort is being made by the Bureau of Agriculture at Manila to raise the standard of quality for the copra produced in and exported from the Philippine Islands. For some time it has been a matter of no little concern that it has brought a uniformly lower price than that produced in other countries. Moreover, the demand for the low-grade Philippine copra has never been as brisk and constant as that for the high grades produced in other countries.

The bureau has therefore been making an extensive investigation. Copra from various sections of the islands compared with samples from other countries was found to have a higher percentage of water after "drying." In Laguna and Tayabas Provinces, the chief copra-producing section, obsolete methods of preparation continue, the split nuts being placed over a frame made of bamboo with a fire beneath. Copra produced in this way is dark colored and frequently scorched, and generally presents a bad appearance; it retains too much moisture, which subjects it to mold and bacteria. Furthermore, in many sections of the islands the copra growers pick immature cocoanuts, owing partly to the impecunious condition of many of the copra growers and partly to the method of gathering. Many growers are so constantly in want that they gather immature nuts and sell them at very low prices in order to get money for their immediate needs. It is the practice in most groves to remove the nuts from the trees with long poles equipped with loops. These implements frequently bring down the green nuts with the ripe ones, and in order that they be not a total loss they are worked up with the good nuts. The result is low-grade copra.

In many sections of the cocoanut country "tuba" distilleries are in operation. Tuba is a liquor made from the cocoanut palm juice, taken from the stem bearing the blossoms before the fruit is formed. Under normal conditions the manufacture of this liquor is not as profitable as the production of copra, but when the price is low and the demand for a low grade of copra uncertain and fluctuating, it is sometimes found more profitable to divert the groves to the manufacture of "tuba."

COAL GAS RESIDUALS—FELD PROCESS.*

By F. H. WAGNER.

A hundred years have passed since Murdock lighted the city of London with coal gas, and these years have placed gas lighting in the forefront of industrial progress, while their history shows how the proper utilization of by-products can revolutionize an industry. The early years of coal carbonization could depend upon but little assistance from by-product sales in cheapening the cost of production, and not until modern chemistry was called in did residuals make any appreciable change in this condition.

The recovery of the residuals is a very important conservation of resources, and it is one of the principal means of revenue to the coal gas producer, their sale reducing the cost of gas production in a degree corresponding to the efficiency of the recovery methods adopted.

The principal residuals recovered today are tar, naphthalene, cyanogen compounds, ammonia and benzol, and they will be treated in this order in the following pages. The recovery of benzol is confined almost entirely to coke oven plants, where a direct method of recovery is adopted, and to the tar distiller. While the recovery of naphthalene cannot exactly be termed one of profit in a pecuniary sense, its partial removal from the gas is of distinct advantage.

Gas produced by the carbonization of coal is a mixture of fixed gases, vapors of various kinds, and, at times, globules of liquids, held in suspension and carried forward by the gas. These gases also carry forward some solid carbon dust.

The principal fixed gases are hydrogen, H_2 ; methane, CH_4 , "marsh gas"; ethane, C_2H_6 ; propane, C_3H_8 ; butane, C_4H_{10} ; ethylene, C_2H_4 ; small amounts of butylene, C_4H_8 ; propylene, C_3H_6 ; acetylene, C_2H_2 ; carbon dioxide, CO_2 ; carbon monoxide, CO ; hydrogen sulphide, H_2S ; nitrogen, N ; oxygen, O ; and ammonia, NH_3 . The principal vapors in the mixture are benzol, C_6H_6 ; toluol, $C_6H_5CH_3$; xylol, $C_6H_4(CH_3)_2$; carbon disulphide, CS_2 ; and aqueous vapors. These vapors all pertain to substances which are liquid at ordinary temperatures, but the vapors of naphthalene, $C_{10}H_8$, phenols, etc., pertain to substances which become solid at ordinary temperatures, and must therefore, be subjected to special treatment.

Some of these constituents are of inestimable value to the coal gas producer, and consequently the treatment of the gas is of great importance, and should not only consist of a method of cooling the gas, and thus condensing and precipitating the vapors as a fluid, but the method of treatment should be such as to retain in the gas those valuable illuminating constituents which may be lost in the usual condensing plant.

The Feld system of condensation and purification of coal gas embraces successive cooling with a fractiona-

*From the American Gas Light Journal; abstract of paper prepared for 9th meeting of American Gas Institute.

tion of the products. The usual condensing system in coal gas practice embraces a primary condenser, exhauster, tar extractor, secondary condenser, and ammonia washer; the tar, together with quite an amount of illuminants, being removed in a greater measure by cooling, while in the Feld system the gas is not cooled below a point where any volatile hydrocarbons are precipitated or absorbed by the effluent, the tar being fractionated in three washers into pitch, heavy oils, and middle or light oils, and the gas is treated for cyanogen compounds, combined hydrogen sulphide and ammonia, naphthalene, and finally benzol; the entire process carried out in Feld vertical centrifugal washers, as shown in Fig. 1.

The entire condensing plant consists of eleven washers, the first, or pitch washer operating at a temperature of from 320° to 392° F., the gas being kept at this temperature from the hydraulic main by insulating the main and pipe connections, or by the application of external heat; heavy oils from washer (2) being pumped into washer (1) where they are used as the active pitch extracting medium.

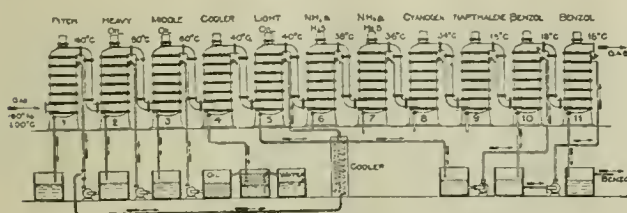


Fig. 1.—Feld Condensing Plant.

Washer (2) removes the heavy oils, and is operated at 320° to 176° F., all operating temperatures being determined from the dew-point of the gas for the constituent to be removed, the extracting medium (2) being the middle oils from washer (3).

Washer (3) removes the middle oils, by contact between the gas and the oils separated by cooling in washer (4); this cooling effected by water the effluent from washer (4) being run into a separating tank where the oil is separated from the water.

The light oils are removed in (5), where the gases are washed by heavy oils previously cooled in a special cooler; the oils from (5) being run into a reservoir from whence they are pumped into the first benzol washer.

The washers for ammonia and hydrogen sulphide operate at from 104° to 97° F., the hydrogen sulphide being combined with the ammonia with the formation of ammonium sulphate. The cyanogen washer operates at about 97° to 93° F.

The naphthalene is removed in (9) at about 65° F.; while (10) and (11) extract the benzol and its homologues, the partially saturated oil from (10) being pumped into (11).

Tar.—Tar is a thick, dark brown, viscid, oily liquid, its chemical nature is very complex, and it contains a large number of compounds. The crude gas leaving

the retorts carries with it a number of hydrocarbon and other vapors, and as the illuminating, as well as the calorific quality of coal gas depends upon its hydrocarbon constituents, it is of prime importance to so treat the gas as to retain as many of these hydrocarbons as possible. A reduction in temperature reduces the hydrocarbons of greater density to liquid form, and this liquid is usually termed "tar." In spite of the fact that the gas temperature at the hydraulic main is perhaps never lower than 145° F., large quantities of tar are deposited at this point, and it is, therefore, almost impossible to retain the hydrocarbons of this class in the gas with the usual method of condensation.

The nature of the coal and the temperature of carbonization exercise a great influence upon the quantity and quality of tar produced, and govern to a great extent, the final cost of gas production.

In the systems applied at present, the removal or the precipitation of tar is accomplished by cooling; quite an amount of condensation occurs between the retort and the hydraulic main, a further amount of tar being deposited in the hydraulic main proper, after which the gas goes to the condensers, where gradual cooling further reduces the tar content. After leaving the condensers, the gas still contains tar globules in suspension, it being possible to remove these last traces only by friction.

In the Feld system, a different method is employed, the heat in the gas being utilized by a system of fractional coolings to separate, or wash out of the gas, tar in its principal constituents. The treatment may be varied to prevent the formation of tar as much as possible, by maintaining the gas coming from the retorts at a temperature above the dew-point of the gas for the constituents of high boiling points. This may be done by covering the connections from the retorts to the first washer with insulating material, or by applying heat to the exterior of the pipes, the gas being led to the washers where it is subjected to fractional cooling and successive washings at successively lower temperatures, so that the various tar constituents are separated from each other by employing the temperature of the gas, and without the necessity of employing extraneous heat after previous cooling.

A Feld washer arranged for hot tar washing is shown in Fig. 2; and in order that aqueous condensation may be avoided, the washing tar should be from 40° to 60° F. above the temperature of the gas at the inlet to the washer, this hot tar being the active tar extracting medium.

A, Pelouze condenser; *B*, gas port in washing chamber; *C*, upper washing chamber; *D*, lower washing chamber; *E*, gas inlet; *k*, tank containing wash tar; *r*, steam coil; *l*, tar pump; *m*, pre-heater for wash tar; *s*, insulated connection from *k* to *l*.

In order to keep the wash tar at the desired temperature the steam pipe *m* is located beneath the pipe *s*. The hot tar is pumped from *k* through *s* and *m* to *A*

and through the overflow pot *u*; any surplus tar overflows at *O* and *p* and returns to tank *k*.

The tar overflows from *A* through *b* and *d*, *e* and *g*, into the upper chamber *C* of the washer, where it is picked up by the washing cones within the chamber and spread out over the entire gas space, the depth of

washer, but it is not always necessary to circulate it through the Pelouze condenser, this omission being dependent upon the condition of the tar in the gas. The amount of hot tar circulated may vary from 0.5 to 2.5 gallons per 1,000 cu. ft. of gas per hour; larger volumes of gas require proportionally less circulating tar than smaller volumes, but the quantity of washing tar must be regulated to prevent the gas reducing the temperature of the wash tar. The wash tar should be pumped through the preheater *m* before it enters the washer, the preheater having a steam coil; and in some cases it may be necessary to insulate the tank containing the wash tar, and also have a steam coil, or radiator, made in one piece in order to prevent leaks and thus mixing water with the tar. Care must be exercised to prevent the deposit of thick tar in the Pelouze condenser, and if the washer should be stopped for any reason, it must be emptied of tar at once in order to avoid cooling the tar and clogging up the passages.

Table I gives the results secured in washing with hot tar, the washer having a Pelouze condenser in one instance, but not in the other.

The Feld process of tar washing was installed in a works in Bohemia in 1907, and the tar was fractionated into pitch, heavy oil and light oil, with the result that the tar produced by the old method of condensation sold for \$5.00 per ton; while with the Feld system producing the oils direct from the gas, the equivalent of this ton of tar sold for \$16.00.

Naphthalene.—($C_{10}H_8$) is a hydrocarbon, melting at 174° , a boiling at 424° F., and it sublimes at lower temperatures. The deposition of solid naphthalene in the mains or apparatus causes many operating difficulties, as it decreases the cross-sectional area of the gas conduits, producing back pressure on the works. Its presence in the gas is probably due to the high heats employed in present day carbonization, causing a partial distillization of the tar with formation of naphthalene. The greater part of the naphthalene produced goes over into the tar, the gas containing only a portion of the naphthalene vapor, its maximum content depending upon saturation at various temperatures; but outside of the temperature of carbonization the naphthalene present in the gas is due to the character of the coal used and upon the time of contact between the gas and hot coke and retort walls. In order to avoid stoppages in the pipe connections due to sublimation, it would be necessary to cool the gas to a temperature corresponding to that of the gas in the buried mains, but as it is almost impossible to always do this, it becomes necessary to remove the naphthalene from the gas by a suitable extracting medium. The best solvents for this purpose are anthracene oil, creosote oil, and water gas tar; tar from vertical retorts has also been used, but it must first be subjected to complete cooling.

If all of the naphthalene were removed from the gas, the latter would suffer considerably in candle-

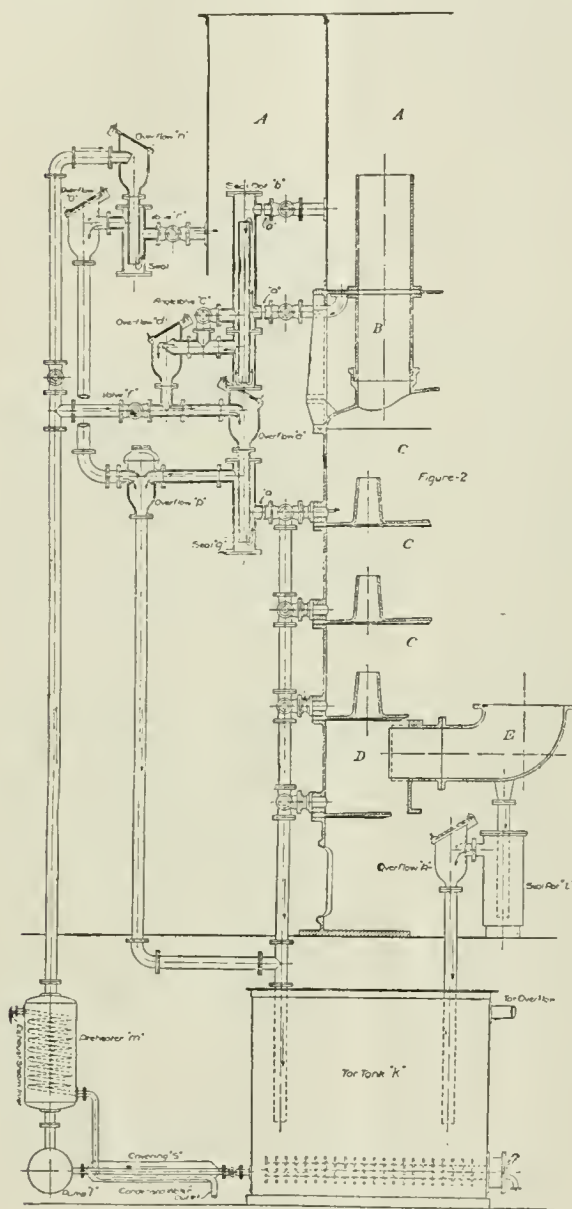


Fig. 2.

the spray being from 8 inches to 14 inches, depending upon the size of the washer. The gas is thus brought into intimate contact with the hot wash tar, and is subjected to a thorough washing, the wash tar and the tar separated from the gas, overflowing through the gas port to the next lower washing chamber; here the wash tar is again circulated by the cones in the chamber, and the total combined tar finally leaves the washer through the pot *i* attached through the gas inlet connection, and by means of overflow *h* enters *k*; the surplus from this tank flowing to the tar storage. In order that the maximum results may be secured, the wash tar should be constantly circulated through the

power, and no more should be expelled than would produce sublimation with consequent stoppages. Under ordinary conditions, 100 grains of anthracene oil will absorb from 10 to 25 grains of naphthalene, according to temperature, but 3 to 4 per cent of benzol should be added to the oil, this addition leading to greater extraction efficiency, which can be further increased by thoroughly and slowly cooling the gas, as the absorption is most complete at 60° to 70° F.

One per cent of creosote oil will, under ordinary conditions, absorb one per cent of naphthalene, by weight, but is dependent upon the amount of phenols present. Water gas tar will absorb from 18 to 20 per cent of its weight in naphthalene, its efficiency depending upon the phenols present. If water gas tar or water gas oil is used it can be run back to storage bearing its naphthalene burden, as the latter is not detrimental to the further use of the tar or oil, but if anthracene or creosote oil is used they can be regen-

from coal gas is not a remunerative proposition for works carbonizing less than 250 tons of coal per day, as the same labor expended on a plant of thin size, can readily handle the proposition in one of double that capacity. The return for a plant carbonizing 250 tons of coal at one works, and 750 tons at another, the sludge from both being worked up one plant, deducting operating expenses, 6 per cent interest and 6 per cent for depreciation, amount to \$27.935 per year without the revenue from the production of ammonium sulphate from the cyanogen press liquor sold on the basis of concentrated ammonia. The extraction of cyanogen in this case shows the life of the oxide is increased 22 per cent.

The two systems of cyanogen recovery that have met with the most pronounced success, are that of Bueb and the one devised by Feld, the former making an insoluble ferro-cyanide coke, and the latter a soluble cyanide sludge.

The Feld process differs from the Bueb in that it is applied after the ammonia has been removed from the gas, this alkali being replaced by milk of lime in the copperas washing medium. The combined solution of lime and copperas is run into the Feld vertical washer, the resultant sludge from the bottom being boiled and then filter-pressed, the product being calcium ferro-cyanide. The product from a Bueb plant is usually worked up into potassium ferro-cyanide, but requires additional apparatus for the removal and concentration of the ammonia carried in the sludge.

Ammonia.—Ammonia results from the union of nitrogen with hydrogen, $N + H_3 = NH_3$; and besides being an important source of revenue, its removal from gas is necessary on account of its destructive influence on the brass and copper of meters and gas fittings; when burned in gas it gives off fumes of oxides of nitrogen. The usual method employed for the removal of ammonia depends upon its solubility in water, at ordinary temperatures water absorbing about 708 times its volume of ammonia gas, the absorption increasing with a decrease in water temperature, or:

One volume of water at 32° F. will absorb 1,050 vols. of NH_3 .
One volume of water at 50° F. will absorb 813 vols. of NH_3 .
One volume of water at 59° F. will absorb 727 vols. of NH_3 .
One volume of water at 68° F. will absorb 654 vols. of NH_3 .
One volume of water at 77° F. will absorb 586 vols. of NH_3 .
One volume of water at 183° F. will absorb 180 vols. of NH_3 .

if the pressure of the ammonia gas is equal to that of the atmosphere and the gas carries no tar.

In American gas works operation the ammonia is removed by condensation and washing, the first portion being removed in the hydraulic main, due to the condensation of water vapors, which absorb ammonia. Cooling the gas in the condensers also causes deposition of water which absorbs more ammonia, the final ammonia being removed in the scrubbers or mechanical washers, using as little wash water as is consistent with the result desired, viz.: strong liquor.

The raw ammonia liquor usually contains from 1 to 2 per cent of ammonia, and is usually worked up for

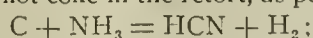
TABLE I.—FELD HOT TAR WASHING—WASHER WITHOUT PELOUZE CONDENSER.

Gas Temperature at Inlet to Washer	Tar Content in Grains per Cu. Ft.		Grains Removed.	Efficiency Per Cent.	Gas Passed Per 24 Hrs. Cubic Ft.
	Inlet.	Outlet.			
131° F.....	11.512	0.2930	11.219	97.46	2,463,000
127° F.....	10.386	0.2160	10.170	97.92	2,453,832
129° F.....	10.818	0.2930	10.525	97.29	2,341,800
129° F.....	13.518	0.4170	12.101	96.92	2,397,000
126° F.....	9.907	0.5250	9.382	94.70	2,400,000
WASHER WITH PELOUZE CONDENSER.					
130° F.....	10.050	0.0436	10.0064	99.56	2,600,000
194° F.....	13.100	0.0872	13.0128	99.34	2,600,000

erated for further use by being distilled and condensed, the naphthalene crystallizing out.

Attempts have been made to use naphthalene as fuel in internal combustion engines with some success. The drawback seems to be that it is necessary to start the engine with gas or some liquid fuel, and to so operate it until hot enough to melt the naphthalene, after which the latter is fed to the engine, vaporized, and exploded. Success in this direction would give another source of revenue to products of coal.

Cyanogen.—Cyanogen (C_3N_2) is probably produced during carbonization in the form of hydrocyanic acid by the decomposition of some of the ammonia by contact with the hot coke in the retort, as per the equation,



and the amount produced bears a certain relation to the nitrogen in the coal. The removal of cyanogen from coal gas is of advantage for two reasons: 1st, because of its corrosive effect on works apparatus; 2d, because it is a valuable by-product, and if permitted to pass into the purifiers, it will combine with the iron in the oxide rendering it inactive for hydrogen sulphide extraction. On the other hand, spent oxide containing a high percentage of cyanogen is more valuable than if it contained only sulphur, as it is often purchased on the basis of its "prussian blue" content, the cyanogen combination.

The revenue derived from the extraction of cyanogen

one of the following products: 1. Concentrated liquor. 2. Aqua ammonia. 3. Sulphate of ammonia. The product recommended for any particular works depending upon local market conditions.

Concentrated ammonia is the raw liquor freed of a large portion of water, and it is used for producing other ammonia products. Aqua ammonia is a solution of ammonia in distilled water, used for cleansing purposes. Ammonia sulphate is produced by distilling

sections having a somewhat deeper seal than the others, in order to permit of more efficient mixing of lime and liquor. A final boiling of the liquor in the lower sections liberates all the fixed ammonia, and the stills should be so operated that the waste liquors leaving the bottom contain not more than 0.005 per cent of ammonia.

If concentrated liquor is to be produced, the vapors coming from the still are washed in a lime washer to remove any carbonate of ammonia that may be formed, after which the vapors are condensed and run into storage.

The earning capacity of a concentrating plant operating in conjunction with a plant carbonizing 300 tons of coal per day should be, with ammonia at 8 cents per pound, about \$25,788 per year, or—

375,000 lbs. of ammonia at 8 cents.....	\$50,000
Labor	\$1,830
Materials	1,922
Miscellaneous	460

Total operating cost, less interest and depreciation	4,212
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Profit per year.....	\$25,788
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If the weak liquor produced in the works can be sold as such, and if the ammonia in this liquor, based on the above prices of concentrate, is worth 6 cents a pound, the yearly gross revenue would be \$22,500, but from this would have to be deducted the added freight due to shipping a larger bulk. In order to make the sale of weak liquor a profitable undertaking compared with concentrate, it would be necessary that an ammonia works be established in very close proximity to the gas works.

If aqua ammonia is to be produced, the vapors from the still are sent into lime washers, coolers, charcoal filters, oil washers, caustic soda washer, and finally into the absorbers.

The earning capacity of an aqua plant of the same size as that quoted above, should be about \$47,030 per year, or—

780 tons of 20° Bé aqua at \$102.....	\$79,560
Labor	\$ 3,630
Materials	7,610
Miscellaneous	21,290

Total operating cost less interest and depreciation	32,530
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Profit per year.....	\$47,030
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If sulphate is to be made from the ammonia vapors, the vapors are sent into the saturators containing sulphuric acid, where the ammonia and the acid combine to form sulphate; and the earning capacity of such a plant, the same size as those above, should be about \$30,809 per year, or—

727 tons of sulphate at \$60.....	\$43,630
Labor	\$ 1,830
Material	10,221
Miscellaneous	760

Total operating cost, less interest and depreciation	12,811
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Profit per year.....	\$30,809
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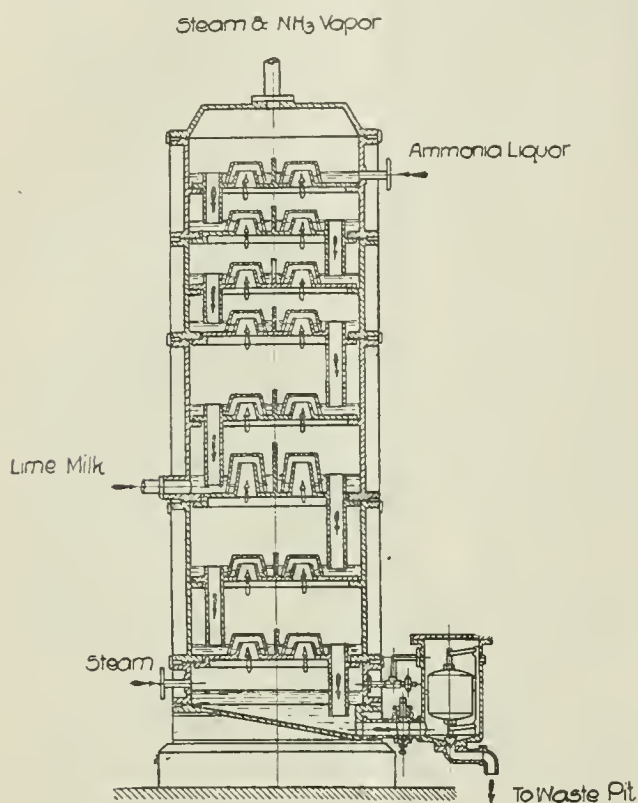


Fig. 3—Ammonia Still.

the liquor, and absorbing in sulphuric acid, by passing the gas through an acid bath, or by combining the ammonia in the gas directly with the sulphur radical, discarding sulphuric acid.

The working up of the liquor is usually effected in continuous stills (Fig. 3), operating by live steam, and as the principle of operation is practically the same in all stills on the market, only one method will be described.

The still usually consists of a series of superimposed sections of cast iron; each section provided with a steam passage in the bottom covered with a hood or bell, and an internal overflow for liquor. The liquor having been heated, enters at the top of the still and flows from section to section; the steam enters at the bottom, passes up through the steam passages, and is made to pass through the liquor by means of hoods or bells. The liquor is thus gradually brought to the boiling point, the free ammonia and other gases mixing with the steam in the upper portion of the apparatus. Milk of lime is introduced in small quantities into the lower, or liming section, the hoods of these

During the last 15 years, the attention of investigators has been turned towards simplifying methods, and instead of treating the gas liquor as in the old or indirect system just described, the endeavor has been to pass the gas directly into and through the saturator, this method being termed the "direct process." Other investigators have proceeded along somewhat different lines, and while passing the gas through a closed saturator, vaporize the ammonia produced by previous condensation and then pass these vapors into the saturator in conjunction with the gas, this latter development being known as the "semi-direct" process.

The Feld system is more truly a "direct process" than any of the methods mentioned as sulphuric acid is not used; and when it is remembered that the pro-

pressor *G*. The overflow from regenerator *B* enters regenerator *C*, where a further treatment with sulphur dioxide is effected, and then enters the wash liquor tank *D*, from whence it is again pumped to the washer. Alternately treating the liquor with sulphur dioxide and with crude gas forms polythionate in the first instance, and thio-sulphate in the second, the polythionate being the active washing medium; an equivalent amount of hydrogen sulphide is removed from the gas in conjunction with the ammonia in the washer.

When the liquor has attained a strength equivalent to 35 or 40 per cent of ammonium sulphate, a portion of this concentrated solution is pumped into the oxidation or finishing tank *H*, it being replaced in the circulating system with weak liquor from prior condensa-

- A-FELD VERTICAL CENTRIFUGAL WASHER
- B-FIRST REGENERATOR
- C-SECOND REGENERATOR
- D-LIQUOR SUPPLY TANK
- E-PUMPS
- F-SULPHUR STOVES.
- G-AIR COMPRESSOR
- H-FINISHING TANK
- J-SULPHUR DRAIN BOARD
- K-SULPHUR CENTRIFUGAL
- L-CLEAR LIQUOR STORAGE
- M-VACUUM BOILER
- N-SULPHATE DRAIN BOARD
- O-SULPHATE CENTRIFUGAL
- P-ROTARY SALT DRYER
- Q-PRECIPITATING TANK
- R-NH₃ STILL
- S-CO₂ SEPARATOR
- T-NH₃ CONDENSER
- U-SUPPLY TANK
- V-UTILITY TANK

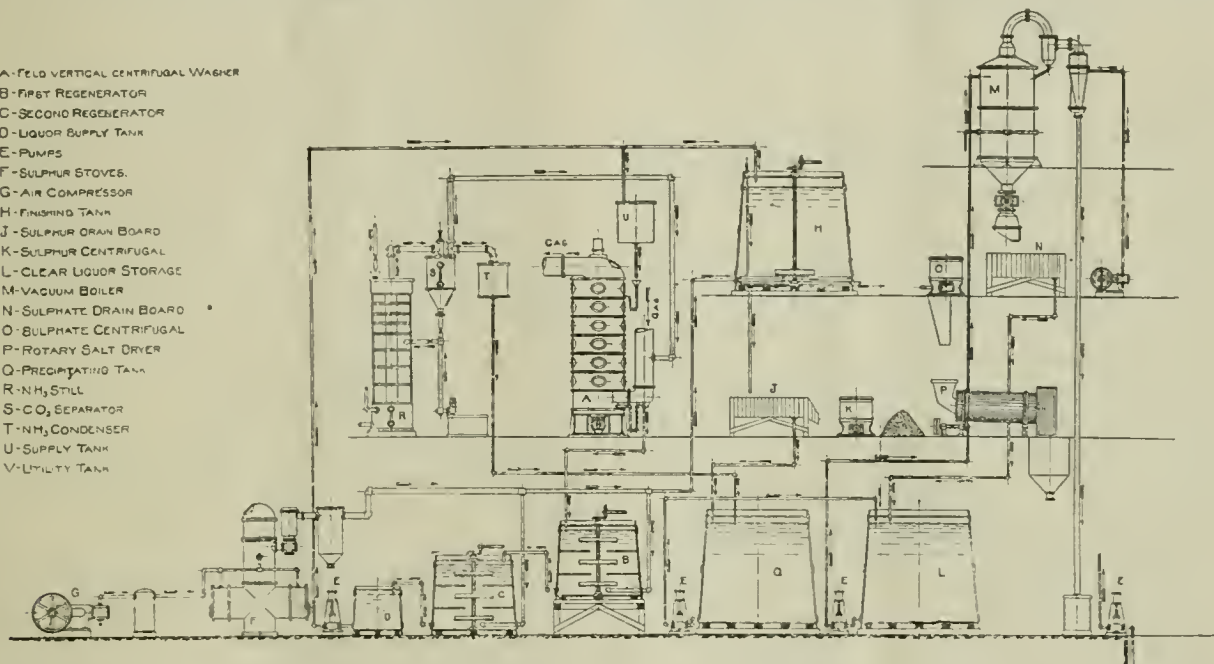


Fig. 4.

duction of one ton of sulphate requires approximately one ton of acid, the importance of this advanced step can be realized. Feld combines the sulphur in the gas with the ammonia thus producing ammonium sulphate by his polythionate process, no other oxydizing agent, except atmospheric oxygen, being required, and the latter is used only in the stove where the sulphur is burned to form sulphur dioxide, this sulphur stove displacing the sulphuric acid factory which has hitherto been necessary.

The method of operation can best be understood by following the diagram. The plant is started by filling the regenerator tanks *B* and *C*, and the wash liquor tank *D* with weak ammonia liquor from the works, or with fresh water; this liquor or water being then pumped into the supply tank *U*, from whence it flows into the top of the washer *A*. Ammonia extraction follows immediately, and the liquor flows from the bottom of the washer as thio-sulphate, entering regenerator *B*; where it is treated with sulphur dioxide coming from the sulphur stove *F*, the dioxide being forced through the liquor by pressure from the com-

pression. In *H* the polythionate liquor is treated with heat from a steam coil, and some sulphur dioxide, if this should be necessary; by this treatment the thio-sulphates are transformed into polythionates, which are in turn decomposed into sulphate and free sulphur. The decomposed liquor is drawn off from the finishing tank onto the sulphur drain board *J*, and the free sulphur, in the form of hard grains, is placed in the centrifugal *K*, where its moisture is expelled. This sulphur is returned to the sulphur stove for the further production of sulphur dioxide. The liquors from the drain board and that from the centrifugal flow to the precipitating tank *Q*, where it is treated with concentrated ammonia, or $(\text{NH}_4)_2\text{S}$ from the condenser *T*; this liquor is then transferred to the storage tank *L* and pumped from there to the vacuum boiler *M*. The concentrated ammonia from the still and condenser is sent into the precipitating tank in order that any iron in suspension may be thrown down, insuring a clean, white salt; the amount of ammonia used for this purpose is very small, but it is all recovered in the sulphate. The liquor is evaporated in a vacuum (an open

evaporator may be used if desired) in the boiler, and the salts are drawn out onto the drain board *N*, and from thence to the centrifugal *O* and rotary dryer *P*, the salts thus produced being ready for bagging and shipping. The mother liquor from the drain board and centrifugal returns to tank *L* and from there is pumped back to the boiler.

The still *R* is used for the purpose of evaporating any ammonia liquor thrown down by previous condensation, these vapors being returned to the gas at the inlet to the washer, a small portion of the vapor being sent into the condenser *T* for producing the $(\text{NH}_4)_2\text{S}$ used in the precipitating tank. If Feld's system of hot tar extraction is installed, a still will not be necessary, as there will be no precipitation of ammonia; neither is a still necessary if the production of ammonia liquor does not exceed the amount of liquor required in circulation.

This process requires but very little expert control, the mechanics attending the machinery being capable of making the necessary liquor tests after a little instruction.

The Bueb process for the extraction of cyanogen produces ammonium sulphate in solution, and therefore, in combination with the Feld explained above, forms a very remunerative proposition.

The income from such a combined plant in a works carbonizing 300 tons of coal per day is approximately as follows:

Cyanogen	128,500 lbs. at 13.25c....	\$17,025.00
Sulphate	1,349,250 lbs. at 3.00c....	40,477.50
NH ₃ in press cake	29,750 lbs. at 7.00c....	2,082.50

Total gross earnings.....\$59,585.00

Operating expenses are:

Materials	\$3,695.00
Steam	1,663.00
Power	2,688.00
Miscellaneous	1,000.00
Labor	2,500.00

Total operating expense..... 11,546.00

Net earnings per year less interest
and depreciation\$48,039.00

Benzol.—While the removal of benzol from gas is not of remunerative interest to the coal gas producer under present standard of gas sale by candle power, it is of interest to the by-product coke oven operator, and as all of the preceding data applies to both of these producers, the method of improving and purifying benzol is herewith included.

Benzol is recovered from coal gas after the tar and ammonia have been removed, and all modern systems are based on the process carried out by Brunck in 1887. The gas is washed in a series of washers with light oil, the oil absorbing the benzol, after which it is subjected to distillations, producing benzol, toluol, xylol and solvent naphtha.

The Koppers Company states that the income from extraction of benzol from the gas produced by the

carbonization of 2,000 net tons of dry coal per day, is as follows:

YEARLY RECOVERY.

Benzol, 67 per cent.....	978,000 gallons.
Toluol, 16 per cent.....	234,000 gallons.
Xylol, 8 per cent.....	117,000 gallons.
Solvent naphtha, 9 per cent.....	131,000 gallons.
Total	1,460,000 gallons.
With a gross income of—	
1,460,000 gallons at 15 cents.....	\$219,000
Crude naphthalene, 330 net tons at \$5.....	1,650
Regenerated acid of 408 Bé., 360 tons at \$6....	2,160
Total gross income.....	\$222,810
The operating expense per year being—	
Raw material, consisting of wash oil, sulphuric acid, caustic soda.....	\$15,000
Steam for distillation, air compressor, loading pumps, acid regeneration and cooling water	15,000
Electric power for water pumps, oil pumps, agitator, illumination.....	6,200
Wages for 3 distillers and 2 helpers.....	5,000
Overhead expenses, fire insurance, maintenance and depreciation, assuming the cost of the complete plant to be about \$300,000...	30,000
Calorific loss of the gas.....	13,000
Total operating expense.....	\$84,200

This gives a net profit of \$138,610 or 46 per cent on the investment capital, and making the cost of producing 1 gal.

$$\frac{\$84,200}{1,460,000} = 5.8 \text{ cts.}$$

This profit is, of course, dependent upon the selling price of benzol and the cost of raw material.

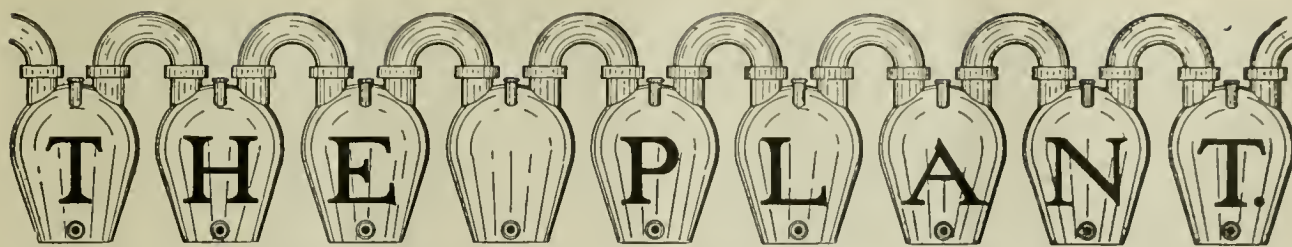
OLIVE CROP OF TUSCANY.

The olive crop of 1914-15 for all of Tuscany, states Consul Benjamin F. Chase, Leghorn, is estimated to average with a tendency to increase, the 1913-14 crop, which, according to last statistics, produced 1,064,000 quintals (106,400 tons) of olives, producing 197,000 hectoliters (5,204,159 gallons) of oil.

The cold winter and dry summer, though having somewhat reduced the very promising crop as to quantity, have much prevented the development and spreading of the olive fly (*Dacus olearia*) and other parasites, and the quality of oil is expected to be superior to that of 1913 as a result.

Very little oil of the 1913-14 crop is still on the market—estimated as not exceeding 5 to 6 per cent of the total production.

The oil from the 1914-15 crop will not be on sale until December or January next, and prices (purchases from the producer) are expected to be about as the last quotation, viz, per 100 kilos (220.46 pounds), 200 lire (\$38.60), for first quality; 180 lire (\$34.74), second quality; 150 lire (\$28.95), third quality; and 105 to 115 lire (\$20.26 to \$22.19), for industrial purposes.



WHY AMERICA DOES NOT MANUFACTURE ANILINE DYES.*

By HARRY McCORMACK.†

There has been so much written and said during the past few weeks on the subject of aniline dye manufacture, that it will probably be difficult to present any new ideas to you. If this is the case, permit me, at least, to hope that the old ideas may be given a new setting.

It has seemed to the speaker that some of the reasons which have been advanced as fundamental ones for our not engaging extensively in the aniline dye industry are, at best, only contributory causes, and are not fundamental at all.

Any one who is a student of economic conditions has observed that there are certain stages in the industrial development of all countries, the stages commencing with the simple industries carried on by a people subduing a virgin land, when the manufacturing industries are limited to those essential for existence, and progressing slowly toward the stage where the industries are extremely diversified, with the raw materials available worked up into the most finished products.

This country, as yet, can be said to be in the early stages of industrial development. Our energies and financial capital have been employed to the limit in such labors as the construction of our railway systems, the building of our large cities, the constructing and operating of street railway systems, waterworks, gas and electric plants, and numerous other utilities which must enter into the growth and life of a new country which is attempting to take on all of the improvements of an advanced civilization. These lines of industry, it has been said, afforded ample opportunity for investment, such investments being secure both as regards principal and as to returns on principal. While such opportunities for investment are available, capital will be very slow to invest in any new lines, particularly such lines as chemical industries which are not very well known in this country and on this account not very well considered as investments by our capitalists. About the only opportunity a chemist has to secure capital for investment is to bring forward some marvelous and secret process to extract gold from seawater, or some process for securing plat-

inum from black sands, or some other project based on imagination.

The development of our railways and public utilities has by no means reached its limit, still affording an opportunity for the investment of our surplus capital, together with much capital coming from European countries. It will therefore be some time before much capital is available for investment in chemical industries.

The mental viewpoint of our nation as a whole has been a handicap to the development of the chemical industry. As a nation we are hasty and impatient. We are not so constituted that we can spend years of research on particular problems as has been the case with the men who have been most successful in bringing forward new chemical processes. Our chemists, mainly, are desirous of working at problems promising quick solution. Our chemists, too, seem to prefer to work on problems which have no utilitarian possibilities. The idea seems to be that it is a disgrace to secure any money for scientific achievement. The chemist has his mind fixed on some "real contribution to chemical knowledge" with the idea that any "real contribution to chemical knowledge" can be of no practical value. Our American capitalist, seeking immediate returns on his investment, has, on the other hand, the dollar under such close focus that only a high power objective can be used which produces very high magnification. It is, therefore, extremely difficult to bring these two parties, chemist and capitalist together and have them work for the common good.

All industries in this country, chemical as well as others, are still suffering from the idea on the part of the practical man that the scientist possibly may be of use to teach his theory to someone who has no more important work than to learn this theory, but can be of no possible use to the practical man. On the other hand, the scientist has a poor opinion of the brains of the practical man thinking that by accident he has been able to accumulate some money, but so far as being of any practical value to the world—certainly not. He has contributed nothing to the advancement of human knowledge. The attitude of both must change, and each must be willing to admit the need of the other before we can secure the desired industrial advancement.

This viewpoint in some of the European countries, particularly in Germany is radically different. The chemist in Germany is looked on as one of, if not the principal contributor to the commercial success of the nation. Everything possible is done to aid him in

*Paper read at the November meeting of the Chicago Section of the American Chemical Society.

†Professor Chemical Engineering, Armour Institute of Technology.

his work. There is a close connection in Germany between the college professor or instructor, and the establishment having the need of expert chemical knowledge and advice. Indeed, many of the men connected with large universities are also engaged in research problems brought up by some manufacturing establishment. They receive from their college connections sufficient salary to enable them to live, and receive from the manufacturing establishment a small salary with the understanding that when any processes are brought out of commercial value a portion of the proceeds will go to the discoverer. This arrangement, it is believed, has contributed more than any other one thing to the success of Germany in the establishment and enlargement of all her chemical industries, particularly of the aniline dye industry.

While we are speaking of the aniline dye industry and commenting on Germany's success in this line of chemical endeavor, we must not forget that the aniline dye industry originated in England and that for several years England enjoyed a monopoly of this business. Perkin, an English chemist, in 1856 prepared the first coloring material from coal tar. The first color prepared was mauve. This was followed by a number of others brought out in different years, extending from 1856 up to about 1867. All of these dyes were new materials so were not attempts in any way to duplicate coloring materials at that time on the market, the principal dye stuffs at this time being of vegetable origin and none of them being prepared synthetically.

The two chief vegetable dyes in use at this time were alizarin prepared from madder, and indigo prepared from the indigo plant. About 1869 the Germans commenced to be interested in the production of synthetic dyes. Unlike the English they were not content in preparing new dyes which would find probably a very limited market at least for some time. They however, attempted the synthesis of the dyes which were then most in demand. Graby and Liebermann, in 1869, succeeding in synthesizing alizarin, starting with anthracene as the raw material. This dye stuff, when put on the market, of course, had to meet at once the strong competition of naturally prepared alizarin. Their work, however, has been so thoroughly done, that it was able to meet this competition and the sales of the natural product fell off very rapidly.

Following the success of these investigators on the synthesis of alizarin, came the work of Beyer on indigo. About 1880 Beyer had succeeded in synthesizing indigo. His indigo synthesis at this time, however, was not a success as his raw materials were too costly and the yield too low. He was, however, able to sell his patents to the Badische Anilin Company for about \$100,000 and from these patents they received no practical benefit. This, however, did not deter them from purchasing in 1890 the patents of Heumann for the synthesis of indigo, starting with different raw materials and conducting the synthesis in a different man-

ner. Heumann's synthesis enabled the manufacturers to make use of naphthalene, a very cheap and abundant coal tar product, as a basis for their indigo synthesis. It is true, however, that the first step in the production of indigo from naphthalene was not brought out in the original process, but was discovered some years later. Long years of experimenting on the part of these German chemists was rewarded by the successful commercial outcome of both of these syntheses on alizarin and on indigo. Practically both the natural products have been driven from the market by the artificial ones.

England, who commenced the manufacture of these coal tar dyes, has lost this business to such an extent, that we hardly think of England as entering into the production of coal tar dyes at all.

There must, therefore, be some reason why England lost this supremacy. We are accustomed to think of Germany as being the originator of the industry but, as has been shown, this is not true. It is the writers' opinion that the prime reason for England losing this great industry is the fact that she had no connection between the industries and the university man as Germany has developed. Therefore, not having the available research talent which is absolutely necessary, no new processes or materials were brought out and the industry therefore died. We, like England, have no such body of research men at the present time who would be available for research service along the lines desired.

Lack of raw materials in this country is also an additional reason why we have no considerable aniline dye industry. With all the other things which are necessary in the building up of a coal tar dye industry, we must have some coal tar. So long as we persist in coking 85 per cent of our coal in beehive ovens where the volatile products are entirely lost, just so long will we lack the necessary quantity of coal tar products for the establishment of the aniline dye industry. In the manufacture of aniline dyes it is necessary that we not only have coal tar, but that we have coal tar in very large quantities. Hausermann estimates that 100 kilograms of tar under distillation will yield:

- .6 kg. of benzene.
- .4 kg. toluene.
- .5 kg. higher homologues of benzene and toluene.
- 8 to 12 kg. of naphthalene.
- 5 to 6 kg. of phenol.
- .25 to .30 kg. of anthracene.

The above would represent products obtained from the coking of 2,000 kilograms of coal. It should also be stated that in the distillation of the tar we get about 30 per cent creosote oils and about 60 per cent pitch. Both of these products must also be commercially utilized if the handling of the coal tar is to be profitable.

We must remember when we are considering the aniline dye industry that it is an industry which deals not only with the products obtained from coal tar, but that it is a very widely diversified chemical industry.

Before these products obtained from the distillation of coal tar are available in any way as dye stuffs, they must undergo many chemical transformations and many chemicals will be necessary in order to bring about these transformations. We find, therefore, that the great German aniline dye companies are also very extensive manufacturers of practically all kinds of chemicals.

You are doubtlessly familiar with the fact that a group of these German companies went to Norway several years ago and purchased the plant and rights of the company operating the Birkland-Eyde patents and commenced the manufacture of nitric acid from the air. You possibly may also be familiar with the developments in this direction since this time; that these companies have developed the greatest group of hydro-electric plants in the world and have gone into the manufacture of nitric acid, calcium nitrate, sodium nitrite, calcium carbide and calcium cyanamide on a scale never before attempted. These Norwegian projects alone have an actual investment of upwards of fifty million dollars.

It is estimated by one of our best informed American dye manufacturers that it would take at least \$400,000,000 to cover the investment in Germany of various German companies engaged in aniline dye manufacture. This gives you some idea of the capital involved in the industry.

To obtain an adequate idea of the industry you should realize, in addition to the amount of capital invested, something of the *spirit* which these men have invested in their industry. This can possibly be best visualized by calling to your attention some of the recent achievements of two of these companies. One of them, as you will remember, recently brought out the synthesis of ammonia after Haber and L'Rossignol had worked on the problem for some ten years in spite of the fact that it had been previously said by many chemists to be unsolvable. The other company, you will remember, gave us the process for the synthesis of rubber, this process being worked out completely to a satisfactory conclusion possibly years before there will be a real commercial demand for their product. You must remember that to have real commercial demand for a product it must be sold at a price to meet all competition. Here they are bringing out an article which will have to compete in price with the natural rubber. They did not hesitate, however, on this account, but proceeded with their experimental work and developed the product their previous experiences with alizarin and indigo having shown them that if you work long enough you can succeed in overcoming even such competition as is to be met in outselling a natural product by an artificial one. Some of our American writers in the past few weeks seem to have forgotten that the aniline dye industry in its early history had to overcome such competition in the line of alizarin and indigo, which was much more strenuous than any conditions which would

have to be met by American manufacturers entering the field with aniline dyes. The writer has an impression of the German spirit in chemical industry which will never be effaced. Dr. Bernthsen at the 8th International Congress of Applied Chemistry, had just concluded his masterly address on the synthesis of ammonia, when Dr. Duisberg, director of a rival German Company, advanced to the platform and proceeded to tell us of the importance of this work and its effects. His attitude was that of a man glorying in the accomplishments of his fellow chemists, even if rivals, and seemed to radiate the feeling that if there was any more important work in the world than that in which he and his associates were engaged, he had never heard of it. When we can secure some such attitude as this among our chemists, our industries will not fail to advance.

Probably the best way to present to you some idea of the things required in the manufacture of aniline dye would be to take a typical product such as indigo, and outline to you the steps necessary in the transformation of the coal tar product to the dye. There are two syntheses being used for the production of indigo; one starting from benzene and the other from naphthalene. As you noted from the table given, naphthalene is much the largest single constituent obtained from coal tar, which is utilizable in dye manufacture. It is therefore the cheapest raw material which can be used for the synthesis of indigo. The process using naphthalene is therefore selected and the steps are as follows:

The Naphthalene is oxidized to phthalic anhydride by being heated with concentrated sulphuric acid and mercury.

The phthalic anhydride thus obtained is converted into phthalimide by heating with ammonia.

The phthalimide on being treated with bleaching powder gives anthranilic acid.

Anthranilic acid on being treated with chloroacetic acid gives phenylglycine-o-carboxylic acid.

The phenylglycine-o-carboxylic acid fused with sodium hydroxide yields indoxyl.

Indoxyl when treated with a large amount of air blown through the solution oxidizes to indigo, the product desired.

It is noticed in this table that in the transformation from naphthalene to indigo, there are seven operations requiring six different chemicals. A manufacturer, to be successful in this industry, would have to be able to supply these chemicals from his own factories and thus be independent in his raw materials. To be successful he would also have to develop a market for the various products he was manufacturing, that is, it would not suffice for him to manufacture these chemicals only in the quantities required in his own plant but to obtain them economically must manufacture them in large quantities and be prepared to sell each and every one of them in the open market.

We should not leave the subject of the aniline dye industry without some comment on the conditions in the industry which are peculiar to this industry. First, the manufacturer must produce many different dyes to satisfy his customers. It is estimated that some 900 different dyes are imported into this country. Second,

he must be continually seeking for new dyes of different shades and of more satisfactory qualities. The manufacturer of dyes, in this way, is not like the manufacturer of, say, steel products. Approximately the same steel products are in style today as were in style five years ago, but in the dye industry, shades which are eminently desired this year may not be marketable at all next year.

Summarizing the reason why we do not manufacture aniline dyes, I would state them as follows:

First, the scarcity of capital available for investment in such industries.

Second, the desire of the American capitalist to secure quick and sure returns on his investments and his inability to see \$2.00 in the distance when there is \$.50 in the foreground.

Third, lack of co-operation between the colleges and universities and our chemical industries.

Fourth, lack of raw materials, due to our waste of our natural resources.

Fifth, our American characteristics of haste and impatience.

Sixth, unsatisfactory patent laws.

Seventh, low tariff on imported aniline dyes.

THE DYESTUFF SITUATION IN AMERICA.*

By ALLEN ROGERS.

Since the outbreak of hostilities in Europe the manufacturers of textiles, leather, paper and dry colors have been very much affected by the shortage of dyestuffs. Many other industries, likewise, are suffering from the lack of chemicals, which have in the past been obtained from Germany. The situation has become so serious that manufacturing associations, scientific organizations and even the public press are giving the matter a great deal of consideration. All this talk has led to more or less confusion and the public at large have a wonderfully distorted conception of the conditions as they actually exist to-day. It is not uncommon to hear the view expressed that it is only a matter of a very short time when the products now shut off will be supplied by American manufacturers. Much as we might like to see such a thing take place, we must not be over confident of its consummation. The establishment of such an industry cannot be of mushroom growth.

Let us look for a moment at the causes which have brought Germany to a position where she controls the dyestuff and chemical markets of the world and from these facts deduce our conclusions. The beginning of the German supremacy in the manufacture of dyestuffs dates back to the discovery of the first coal tar color "mauve" by William Henry Perkin in 1856. As will be remembered Perkin was an assistant to Prof. Hoffmann at the Royal College of Chemistry in London, and while working on the synthesis of quinine,

which by the way has as yet never been made synthetically, he obtained a mass of indefinite composition which colored his towels purple. Although Hoffmann advised him to throw the muck into the sink and stick to the quinine investigation, Perkins was not satisfied until he had eventually separated a definite product which he found could be used for the dyeing of fabrics. Following the discovery, he soon isolated other colors and then tried to interest the English dyers in their application. In attempting to market these products Perkin did not meet with success and in fact he not only failed to arouse the interest of the English dyers, but he lost all of his money and that of his friends in the undertaking. It was not until Hoffmann had returned to Germany and established the industry there that the Englishmen awoke to the value of Perkin's great discovery. Although Perkin was then able to operate a small factory and make good some of his losses, it was too late for England to control the market which by right of discovery belonged to her.

The establishment of the coal-tar color industry in Germany also gave birth to other great chemical industries, which, under the protecting wing of the Government, have grown to such strength that she has been able to defy the competition of the entire world. The German mind, however, should be given full credit for its peculiar aptitude for scientific research. We cannot help but admire the painstaking work which has been necessary to develop such a wonderful industry. We must also admit that many of the greatest scientific discoveries have been made in the German laboratories and universities. Scientific investigation has been fostered by the Government and its application encouraged. The close co-operation between the technical schools, the university, the manufacturer and the government has resulted in a powerful combination which it is impossible to find in any other country in the world.

Should Germany lose in this conflict it would be history repeating itself, for then some other country must take her proud place and dominate the scientific world. Will that country be America? This is a difficult problem to solve as it is only a matter to be settled in the course of future events. Possibly some enlightenment may come from the information contained in the guiding maxim of the Iron Chancellor as stated by himself:

For me there has been but one compass, one pole star after which I have steered; *Salus publica*. Since I entered public life I have often, perhaps, acted rashly and imprudently. But when I have had time for reflection I have always been guided by the question, What is most beneficial, most expedient and proper for my dynasty? so long as I was only in Prussia and nowadays for the German nation. I have never in my life been doctrinaire. All systems by which parties are divided and bound together are of secondary moment. My first thought is of the nation, its position abroad, its independence, our organization in such a way that we may breathe freely in the world. In estimating future events we must keep an eye on the United States of America, for

*Paper presented at the 11th Annual Meeting of the American Leather Chemists' Association, Chicago, Oct. 28, 1914.

they may develop into a danger to Europe in economic affairs, possibly also in others at present wholly unexpected by most of us. In the future the one cannot be separated from the other. The war of the future is the economic war, the struggle for existence on a grand scale. May my successors always bear in mind and take care when the struggle comes that we are prepared for it.

The day has come and so far as Germany is concerned she was prepared, but we in America were not prepared and so as a result, we find ourselves in a predicament which becomes more serious every day. The problems confronting us deserve our most careful consideration. Although personal feelings and selfish motives may make us more or less prejudiced we must eventually be influenced by what seems to be for the best interests of the nation as a whole. What we seek is truth. Let us, therefore, put aside the personal factor and approach the problem with an open mind.

For the sake of argument I should like to put my remarks in the form of a few questions which appear to me to have a vital bearing upon the subject.

1. Have we a sufficient supply of coal tar to meet the demands of an American coal-tar color industry?

In answering this it might be of interest to note the yearly consumption of distillation products in the United States:

	Estimated use in the U. S. A., Lbs.	Tar required, Gals.	Coal necessary, Tons.
Benzol.	15,000,000	600,000,000	60,000,000
Phenol.	8,000,000	160,000,000	16,000,000
Aniline.	3,000,000	100,000,000	10,000,000
Naphthalene.	10,000,000	14,000,000	1,430,000

The table furnished by the courtesy of Mr. S. R. Church, of the Barrett Manufacturing Co. gives us some idea of the tar required to supply even our present market. As tar contains only about 10 per cent of dye forming material it will be seen that something must be done with the other 90 per cent. In this country we are ahead of Europe in working up this residue so have nothing to fret about in that regard. The reason that American coal tar has not been worked up into dyestuff materials is simply because there has been no demand. Should the demand arise, there is no question but that the products could be supplied. Even if one of our great steel corporations should save the benzol they are now burning under their furnaces or allowing to escape into the air, we would have all of the benzol needed for an American coal tar industry.

2. Assuming that we have the requisite amount of coal tar; have we the necessary interlocking chemical industries to make the undertaking a success? It has been claimed that on account of the close co-operation and interdependence of the German chemical factories, what is a waste product in one becomes the raw material for another. For this reason it would appear that we could not compete. Such an argument, however, is too far fetched to warrant serious consideration. The same condition exists all over the world. That is, one factory makes certain products which are used by others, while in return the first concern purchases cer-

tain products from the latter. The interchange of products is made easy in Germany on account of short hauls, but even this is not an insurmountable difficulty. That we do not have the interlocking chemical industries is of course a fact, but what is more to the point we do not even have the main chemical industry depending upon these interlocking chemical industries.

The growth of the coal tar chemical and color industry in Germany has been slow for the reason that it has been in the making. With the knowledge, however, that we possess today such growth would be far more rapid. It is not, therefore, a matter of the raw materials, neither is it a matter of the interlocking chemical industries or the slow growth of an industry that prevents us from increasing our dyestuff and chemical plants. But what we must consider most is that the manufacture of dyes and other coal tar chemicals in Germany is a tremendous industry, controlled by a powerful combination which in this country we would call a trust.

3. Granting that we have the supply of raw materials, will it be possible for us to develop the interlocking chemical industries and the manufacture of dyestuffs in the face of these well established industries in European countries?

In discussing this question there are many problems involved, none of which can be settled by a wave of the hand. Chief among these problems is the outcome of the present struggle. Should Germany be invaded, there is little doubt that her factories would be destroyed. The industry then would be open to the world. Should she resist invasion, it then becomes a matter of finance. People who would be in a position to finance a big industry will hesitate about going into a business which is so uncertain as this is at present. When the war is over German manufacturers will be anxious to convert their stock into cash and will be very apt to do so regardless of the value of the product. This policy, which would be a death blow to any infant industry would not be a new practice by any means. What has been done in the past to crush competition will be repeated. Even at present the embargo on intermediate products is solely for the purpose of preventing American manufacturers from gaining a foothold in the dyestuffs industry.

4. Will it be possible for Germany to furnish the same amount of dyestuffs when hostilities have terminated as she has in the past?

Granting that Germany is not invaded, there seems to be no doubt that she can furnish just as much material as in the past. Her research laboratories may have to be closed for the present, but her factories will no doubt continue to operate.

5. Have we a sufficient number of technically trained men to carry on such an industry?

This question can be answered in the affirmative. We have not an army of research chemists, but under

the circumstances the need is not for new colors, but for those in common use. It is probably true that we could not manufacture so economically on account of lack of experience, but a chemical compound whether made in Germany, France, Japan or America is always the same.

6. What will our universities and technical schools do to train young men for such an industry?

The tendency of modern education is toward the industrial application of science. Many of the old line universities still hold that we should study science for science itself, but these are now in the minority. Courses in Chemical Engineering and Industrial Chemistry are springing up all over the country whose aim is to approach problems from the purely practical standpoint. More such schools are needed even though a dyestuff industry on a large scale is never established. Those that we have are here to stay and those to follow will find a hearty support. Europe has been in the lead so far, but the time has come when we are beginning to see the light. As the demand increases we will find the technical schools ready and willing to meet the issue.

7. What should we do with our patent laws?

We read in nearly every paper on the present situation that our patent laws are of no help to American interests. We read always about the "working clause." It is usually claimed that we should have a working clause so that foreign patents would have to be worked in this country. As I understand it, the working clause does not make a man work his patent in some other country unless a native of said country should want to make the article. To get around this difficulty an inventor can sell a license to some one in that country. England and France have a working clause and they are in as bad a fix as we are in America. So far as our relations with Germany are concerned we have an agreement that the law does obtain in the case of American patents. This might appear at first glance that Germany has the best of the bargain as we hold no dyestuff patents in Germany while she holds many dyestuff patents here. But we must not forget that we have ten mechanical patents to one dyestuff patent which would be seriously affected by breaking this agreement. Further than this practically all of the patents on the common dyestuffs have expired and all of the others will have expired long before we would be in a position to make them. So let us as chemists give that poor patent law a needed rest.

8. What should the government do to protect American enterprise?

The question involves more or less politics, but it is evident that if we are to have a coal tar color industry some one will have to pay the fiddler. It is true that just at the present time those who are in need of colors will promise to do anything in order to get dyestuffs, but when the normal conditions come again they will

forget all about this and then buy where they can get the best figure. If we are to establish an industry of this kind there will have to be some kind of protection more effective than at present. A duty of 30 per cent is now imposed on certain kinds of dyestuffs, while others come in free. To my own mind the suggestion that all dyes be given the same rating and an additional specific duty be added seems very wise. For example, a dye selling for 15 cents pays a duty of $4\frac{1}{2}$ cents. A foreign manufacturer can pay such a duty, but suppose that he has to pay a specific tax of 5 cents per pound also? Will that cut into his profits? A specific duty would be of no value on the more expensive dyes, but then we have the *ad valorem* of 30 per cent for the protection of the American manufacturer. The "Anti-Dumping Clause" is another very important factor in this connection.

At the present time we are making about 100 different dyestuffs in this country. These are not made in sufficient quantities, however, to satisfy the market, but it shows one thing and that is that it can be done. Of the \$13,000,000 worth of coal tar colors consumed in the United States during the year 1913, \$10,000,000 worth were imported and \$3,000,000 worth manufactured here.

It might be said that after all the situation is not so serious as it has been painted. From the point of dyestuffs alone it may not be so serious, but the point is that a small amount of color will hold up a big industry. If we are to become interested at all in an American coal tar color industry it is for the sole purpose of making our country self sustaining in a crisis like the present.

In all that has been written about the dyestuff situation very little has been said in regard to the importers. These men have done a service to the country which very few people realize. They have used every means possible to secure enough color to keep their customers going and have in no case advanced the prices. When the supply in stock became exhausted they used every means possible to get dyestuffs into the country in neutral bottoms. One man, Mr. H. A. Metz, has gone so far as to charter a ship with one of the other color houses, which is now on its way to Germany. This ship is sailing under the American flag and it is hoped that her mission will be successful. If this ship secures a cargo of dyestuffs it will very materially help to tide us over the present difficulty. Even this will not solve the problem, but at least these men should be given credit for what they have done.

Let us bear in mind that our textile manufacturers need dyestuffs; that our tanneries will need colors, that many other industries are directly dependent upon dyestuffs for their existence. And above all that, we have a great many more gray haired men and women in America than we did before the outbreak of the present war.

EXPANSION OF CHEMICAL AND DYE-STUFF INDUSTRY IN UNITED STATES.

On Oct. 15 a committee was appointed by the chairman of the New York section of the American Chemical Society to investigate into the feasibility of expanding the chemical and dyestuff industry in the United States. This committee consisted of Bernhard C. Hesse, chairman; L. B. F. Herreshoff, H. A. Metz, I. F. Stone, D. W. Jayne, J. Merritt Matthews and Allen Rogers. On Nov. 6 the committee submitted its report together with its recommendations. This report, with the exception of the introductory paragraphs, was as follows:

Your committee has carefully considered all the public suggestions as to methods of improvement and has searched through the governmental regulations of the belligerent nations as to embargo and as to contraband of war, in order to construct therefrom a list of chemicals, inclusive of dyestuffs, which have thereby been shut off from the United States, in the hope of thus being placed in a position to make specific recommendations of value.

It can be fairly stated that, in general, the chemical industry of this country is efficiently exploited and is making full use of all the opportunities presented to it under the normal conditions existing prior to the state of hostilities. Some of the chemicals which are imported from abroad are made in considerable amounts in this country as well, and the amount imported under normal conditions depends upon the ordinary normal fluctuations of business conditions both here and abroad. With the stoppage of this foreign supply the domestic production was not at once capable of making up the deficiency, but in a number of instances the American manufacturers have taken steps to increase their capacity, and the strain in the market of those particular things will exist no longer than it will require to extend the manufacturing facilities to the proper extent.

Among these are ammonia salts, barium chloride, barium nitrate, bleaching powder, sodium cyanide, yellow prussiate, sodium nitrate, sodium hydrosulfite, zinc dust.

If, however, it be desired and if public necessity requires the introduction of the manufacture of explosives and further chemicals and dyestuffs into our home industry, such as coal-tar product explosives, pharmaceuticals, medicinals and other intermediates and finished coal-tar dyes, then alterations of our tariff law are inevitable, and the consumers in the first place and the public in general must share in the burden thus imposed. If conditions of national defense in case of attack by a foreign power require us to manufacture our own explosives, and to be in that regard independent of all foreign nations at all times, or if our textile industries or any other of our industries requiring coal-tar chemicals, such as dyestuffs, shall forever be protected and made independent of foreign nations for the

supply of those materials, then the nation as a whole must bear the burden incident to such expansion. Under existing circumstances private enterprise and private capital have gone their limit. They have reached the limit for two reasons:

1. The explosive, dye and similar industries abroad, just referred to, are in a state of high development and of refined organization, and are financially the best suited to carry on an offensive campaign against any nation attempting to take business away from them.

2. Domestic manufacturers are prohibited by law from making use of co-operative commercial devices, such as pools, trusts, manufacturing and selling agreements, and the like, whereas, such devices are wholly lawful abroad, and are encouraged by the respective governments. In other words, the American chemical industry is expected to cope with the foreign industry while both its own arms are tied behind its back and its opponents have full and free use of their arms.

Anti-Dumping Clause.—The remedies required would be an effective anti-dumping clause that would certainly prevent underselling of domestic manufacturers in the United States by unfair methods. What the form of such clause shall be is a problem with which your committee is unable to cope: it is strictly a law-making and law-enforcing problem, and is allied to the usual problem of determining undervaluation as heretofore carried on by our Treasury Department; it, however, is a much more refined problem than the older problem of proving undervaluation. Nevertheless, your committee believes that with such a mechanism in our law that much would be done toward encouraging our chemical industries.

To Create Coal-Tar Chemical Industry.—According to the best information that your committee can gather, such an anti-dumping clause alone would not be sufficient, however, to create complete and independent domestic coal-tar explosives, dyestuffs and medicinals industries. It has been conclusively demonstrated during the past thirty years that the present tariff rate of 30 per cent on dyestuffs is not sufficient to induce the domestic dyestuff industry to expand at a rate comparable with the consumption of dyestuffs in this country, and that therefore all dyestuffs made from coal-tar, whether they be aniline dyes or alizarin, or alizarin dyes, or anthracene dyes or indigo, so long as they are made in whole or in part from products of or obtainable from coal-tar, should all be assessed alike, namely, 30 per cent ad valorem plus $7\frac{1}{2}$ cents per pound specific, and that all manufactured products of or obtainable from coal-tar, themselves not dyes or colors and not medicinal, shall be taxed 15 per cent ad valorem and $3\frac{3}{4}$ cents per pound specific.

Tariff to Aid Dye Industry.—The best information and judgment your committee can obtain is that the above manufactured products of coal tar, not dyes and not colors and not medicinal, should carry one-half the duty of the finished coal-tar dye and that the

above rate of 30 per cent ad valorem and $7\frac{1}{2}$ cents specific would probably be sufficient to encourage and enable domestic manufacturers to expand their operations to such an extent as to supply a very material increase in, if not the whole, of these commodities consumed in this country. The reason for a specific duty is to protect the domestic manufacturer in the manufacture of the relatively cheap dyes, such as the cheap scarlets, the cheap yellows and the like, whose prices abroad are in the neighborhood of from 12 cents to 20 cents per pound, with dyes of that type 30 per cent ad valorem would not offer so serious an obstacle to importation and underselling thereof as does the $7\frac{1}{2}$ cents per pound specific; on the other hand, on dyes whose prices are \$1 and upward per pound the function of the $7\frac{1}{2}$ cents specific more nearly approaches zero. That is, with the cheap dyes the chief function lies in the specific portion of the duty, and with the expensive dyes the chief function lies with the ad valorem portion of the duty.

This is said to be the price the nation will have to pay to have a complete self-contained and independent coal-tar chemical industry. However, it must be remembered that if such an industry be created and importation of coal-tar products, inclusive of intermediates and dyes, is restricted, its ultimate effect upon the Federal revenues will have to be considered. It will, therefore, be necessary to determine carefully if the advantages to be gained are equal to the price to be paid.

Patent Laws.—This committee is a unit in the belief that an alteration of our patent laws aiming at compulsory working or compulsory licensing would not be any substantial benefit to this industry or to the country as a whole. Twenty-nine countries have attempted compulsory licensing clauses and fifty-six countries have attempted compulsory working clauses, and the best information your committee can obtain is that in none of these attempts has there been any appreciable measure of success. While it may be true that under extraordinary conditions, such as now exist, compulsory licensing might have some advantage, yet it is equally true that in normal times the disadvantage due to compulsory licensing or compulsory working would more than over-balance any advantage at all likely to be obtained under stress of unusual conditions.

In none of the countries where there have been working or licensing clauses, or both, co-extensive with the existence of the coal-tar chemical industry has there been established any real coal-tar chemical industry and your committee does not feel that an alteration in our present patent laws could be made which would be effective against foreigners and at the same time not be onerous and a hardship to domestic inventors. Your committee believes that in the long run and in the final outcome, our present system with regard to working and licensing is as efficient as that of any other country. In the dyestuffs industry in particular

there are so many non-patented commercial products and so many commercial products once patented now free from patent restraint that their production alone would form a basis for a very considerable industry, and your committee feels that the way to encourage that industry, if the establishment of that industry in this country be a national necessity, is through a change in the tariff and the additional anti-dumping feature in the administration of the tariff and not through any change in the patent laws. Once established, such an industry could develop and ultimately cope with any foreign combination upon fair and equal terms. Over 90 per cent of the tonnage and of the individual dyes used in the United States will be free from any patent-restraint within the next four years; over 75 per cent of the dyes are now in that condition.

Availability of Raw Materials.—The best information your committee has so far been able to gather is that this country can produce so-called coal-tar raw material in amounts sufficient for the needs of a complete domestic coal-tar chemical industry, inclusive of explosives and dyes, provided there is a certainty of outlet as to volume and continuity. Those engaged in manufacture here do not want to expand unless the dye-users are willing to make corresponding contracts. In other words, it is a closed circle. If the dye-users will contract sufficiently with the dye-makers, the dye-makers will contract with the coal-tar distillers and the industry will take a start. The initiative rests wholly with the users; if they cannot afford to contract the dye-maker and the distillers cannot afford to make their contracts and additional investments.

Coal-Tar Products.—Benzol, toluol and the like are produced in sufficient amount in present installations of by-product coke ovens to provide all of these things that would be needed for a coal-tar chemical industry of a magnitude sufficient to supply the United States market; the separation of these materials from the gas that carries them is dependent upon the market and the demand therefor. There is no inherent defect in our coke industry with regard to the actual making of these things; the only question involved is whether it be more profitable to burn the benzol, toluol and the like contained in the gas as a fuel than to separate them and from each other for purposes of sale. Ample supply can be provided before any plant that could use benzol and the like for dyestuff making could be erected in the United States and thereafter the supply of these materials can readily be kept up to any requirements.

The materials of the preceding paragraph are the ones used in the coal-tar explosives industry, as well as in the coal-tar medicinals and dyestuffs industries. Each of these three industries co-operates with the others to make full use of those materials, alone none can fully make use thereof nor succeed; the correct and proper utilization of these materials requires successful co-existence of all three industries in one and the same country.

Naphthalene and anthracene are contained in the tars produced in the United States in an amount sufficient for the needs of a domestic dyestuff industry, and it is merely a question whether it is more profitable to leave them in the creosote oil, where they now occur, or to separate them out of such oil and refine them for purposes of dye manufacture. Ample supply of either of them could be produced and provided at the same time or shortly after any plant could be erected in the United States for the use of these things in the production of dyes.

What has been said with regard to the supplies of naphthalene is also true of the supplies of cresole.

All the creosote oil contained in the total amount of coke-oven tar now made is separated from it and used. Increased production of creosote oil requires a greater production of tar, and a greater production of tar is dependent upon increased installation of recovery coke ovens.

Phenol or carbolic acid supply is primarily dependent upon our deliberately selected method of coal treatment; to change that treatment so as to get more phenol would entail abandonment of other advantages which would not be compensated for by the increased amount of phenol so produced. Under present circumstances freights and haulages play an important part. At isolated plants, separated by considerable distances from each other, small amounts of phenol are produced, and the separation of the phenol at such individual places would be economically unprofitable, and in order to concentrate this amount of phenol to or at a point where separation could be conducted profitably would entail freight haulages much in excess of the value of the phenol that would thus be transported.

The only source of phenol in sight is that produced synthetically from benzol by means of sulfonation and subsequent melting with caustic soda; this depends in turn upon our benzol supply, and would be profitable only so long as the United States market is not killed by the dumping of foreign phenol thereon, whether such phenol be synthetic or distilled.

Salicylic production depends upon availability of phenol, and the production of benzoic acid depends upon the availability of toluol, which has heretofore been discussed.

Phthalic acid made from naphthalene by means of bichromate cannot successfully compete with the mercury and sulphuric acid process, which is protected by patents having about three years more to run.

Miscellaneous Chemicals and Raw Materials.—Acetic anhydride can be made without trouble in this country, and will be made in this country so soon as the domestic demand is large enough and steady enough to warrant the installation of a suitable plant.

Nitric Acid.—All countries with the exception of possibly Norway and the countries importing from Norway are dependent upon Chile for the raw material for making nitric acid. It will not be profitable to

make nitric acid from air in the United States until the value of the electric horsepower reaches a level of \$3 or \$4 a year, as it is in Norway.

Ammonia and its salts all depend upon recovery coke ovens, and such recovery plants are increasing as fast as circumstances will permit.

Barium chloride and other compounds of barium may be made from domestic barytes. A number of attempts have hitherto been made, but with indifferent success. Factories established within the last year promise to be successful.

Magnesium chloride of a sufficient purity to be used in the production of flooring is almost generally made from magnesite found in Greece, which is the only deposit known having sufficiently high purity; there are reports of suitable deposits in California and in Lower California, and with the completion of the Panama Canal the question of freights, which seems hitherto to have stood in the way of developing these deposits, may be eliminated. Other sources, less remote from centers of consumption, and using other materials, e. g., brine waste are about to be successfully operated.

Manganese in the form of pyrolusite is not known to occur in paying deposits in the United States; these are practically all in the Caucasus.

Potash.—In view of the great exertions that have been made for a number of years, both on the part of the Federal Government through a number of its departments and a great many different groups of capitalists, there is nothing to be said in this report that would be of any value with regard to increased production of potash either as fertilizer or as a chemical.

Yellow prussiate and sodium cyanide can be and have been made from domestic materials in such an amount as to provide practically the entire consumption or a great portion thereof in this country so long as there was a sufficient duty on them; the present duty is not enough to protect the American manufacturer, and those who were engaged therein have in large measure withdrawn from the business, but some are reported to be taking up manufacture cautiously and in limited amount.

Hydrosulphites in solution can be made from domestic materials without interference with any patent rights; the production of solid salts and derivatives are, however, still protected by patents that have a few years more to run.

Sodium nitrate is produced more cheaply as a by-product in Norway than it can be produced anywhere in the world; unless the price of the electric horsepower in this country sinks to a \$3 or \$4 level per year, as in Norway, this product cannot be manufactured in the United States.

Oxalic acid is and has been made to some extent in this country, and the information coming to your committee is that suitable efforts are being made to expand the capacity of existing plants.

Tartaric Acid and Citric Acid.—To make this country independent of others with respect to tartaric acid

and citric acid would call for radical changes on the part of our grape growers and our lemon growers as to the policy of their business.

It is probably true that edible grapes do not produce argols (the crude material for tartaric acid) very largely, and that our domestic lemons do not produce as large yields of juice (the crude material for citric acid) nor as high an acidity as do the Italian lemons; therefore an independent supply of the raw materials produced in the United States for tartaric and citric acids is in the first instance an agricultural problem, and in the second instance a market problem.

General Remarks.—Finally, it should be pointed out that the United States is by no means the only country whose chemical and allied business has been strained or upset by the European war. Each and every other country has felt the strain. British committees have gone into this same subject of expanding British chemical industries, and not only that, but also into the question of making their very basic necessities, and the reports have so far been adverse to any immediate relief by domestic manufacture. The Boston Chamber of Commerce, through its committees, has arrived at the same conclusions for this country.

It is further clear that the stability of a complete domestic chemical industry, in so far as it depends upon foreign supplies, is bound up to a successful merchant marine and to an efficient foreign banking condition just as is all our foreign business.

Findings.—Your committee finds as follows, as to the facts:

1. Prior to the hostilities domestic chemical industry was utilizing and exploiting every reasonable opportunity to its full extent.

2. Since the outbreak of hostilities domestic industry has increased its output just as fast as physical means could be provided and physical obstacles overcome.

3. Since the outbreak of hostilities domestic plants that had theretofore been shut down or partly dismantled because of disastrous foreign competition are said to have resumed operation, with caution.

4. That a 30 per cent duty on some coal-tar dyes for over thirty years has not produced a real coal-tar dye industry in this country.

Conclusions.—Your committee submits its conclusions as follows:

- A. To prevent the unfair underselling alleged to be practiced by foreigners in this country, the adoption of an effective anti-dumping clause.

- B. The so-called coal-tar "intermediates" which are the basis of the coal-tar chemical industry, inclusive of explosives, medicinals and dyestuffs, should be assessed one-half of whatever the finished dyes are taxed for tariff purposes; all coal-tar dyes without exception to be taxed alike, namely, 30 per cent ad valorem and 7½ cents per pound specific.

- C. Changes in the patent laws such as by compulsory licensing or compulsory working clauses are

wholly ineffective, do more harm than good and should not be attempted.

Your committee recommends that this report be submitted to the appropriate committees of Congress. Further, that this report be forwarded to interested parties.

THE DEVELOPMENT OF OUR CHEMICAL INDUSTRIES.*

By GASTON DU BOIS.

If we examine the exports of chemical products from the United States we find that the products exported such as crude oil, benzine, kerosene, lubricating oils, cottonseed oil, animal fats, oleomargarine, acetates, mineral paints, turpentine and rosin, phosphates and metals are practically all products derived from the natural resources of the United States and in the manufacture of which comparatively very little chemical skill is involved. The success of these industries is due more to the mechanical engineering skill in solving the mechanical problems arising in the manufacture than to chemical research. These industries did not require protection by high duties, or at any rate not to the same degree as the manufacture of products of other branches of organic chemical industry; they found a ready market not only in this country but also abroad.

The effect of the war on these important chemical industries of the United States must be very great in as much as Europe is unable to buy these products to the extent it did before, owing to the closing down of many factories and also to the difficulty of shipping to all points of Europe. If we, on the other hand, compare these exported products derived from the natural resources of this country, with the chemical products which are imported from Europe, which amount to probably more than \$100,000,000, of which about \$40,000,000 from Germany, we find that the greater part of these imported products require for their manufacture great chemical skill.

Those of us who have had occasion to examine more closely some of the processes of manufacture developed abroad of the more complex synthetic organic compounds, cannot fail to be impressed by the ingenuity and great resourcefulness displayed by the technical chemists there. The success of those chemical industries represented by our imports was due to the chemists and to their search work along chemical lines, more than to success in solving mechanical problems. These products which we are importing are mainly synthetic dyes, pharmaceutical products, essential oils and synthetic perfumes and also the long line of so called organic intermediate products, which are the compounds obtained by chemical transformation from compounds contained in coal tar (but not themselves

*From a paper presented Oct. 12 at a meeting of the St. Louis Section of the American Chemical Society.

dyes). Therefore with the exception of potassium compounds the products imported are manufactured articles which are not derived by simple methods from natural products.

The manufacture in this country in competition with Europe for those products enumerated above as being the main chemical products imported into this country, has already started and it is in some cases developing. However, it is very much more difficult to foresee how the war will affect these manufactures as, even though competing with Europe, they are nevertheless in many instances dependent on Europe.

It is a fact that Germany practically controls the market in what I called above the "intermediate products" of the large coal-tar industry. In order to give a clear idea of what I mean by "intermediate products" I will mention here a few of the most important.

Aniline oil and derivatives, nitrobenzol and derivatives, toluidine, nitro-derivatives of toluol, beta naphthol and naphthylamin, resorcin, phthalic acid, phenol derivatives and also the various cresols and derivatives. The manufacture of these products developed gradually in Germany and with very little outside competition to contend with; the many hundred products belonging to this class are so dependent one upon the other, their manufacture so interwoven, the production of one being impossible without the production of many others and therefore the necessity of having to find uses and markets for several products, that the manufacture of these intermediate products has never been able to obtain a foothold in this country. The situation has very often been defined and as many times misunderstood, when demands for protective duties on certain classes of goods were made and often refused for reasons which showed clearly that the situation was not understood by the legislators or their advisers, and mostly indicating that the development of these industries was, in the opinion of some legislators, of very secondary importance and should be sacrificed in order to carry through general principles which were more popular.

Industries are not created in one day nor in one year. It took the Badische Anilin and Soda Fabrik 20 years of patient research work, carried out in well equipped laboratories with all facilities and large funds to draw from, to devise a satisfactory method of manufacture of artificial indigo. Would this German firm have undertaken to solve this tremendous problem, if some other factory had already solved the problem at the time the Badische started its investigations?

The manufacture of the coal-tar intermediate products is a far greater problem than the manufacture of indigo and the American manufacturers undertaking their commercial production without protection could be compared to an army trying to build fortifications while exposed to the guns of a hostile army.

It should not be overlooked that developing the coal-tar industry is in line with the preservation of the

natural resources of the United States, and just as well entitled to government protection as is the preservation of our forests, coal supplies, etc.

Another factor which has retarded the development of the coal-tar industry and the manufacture of the intermediate products resides in the great demand for the unrefined products of the coal-tar distillation. The coal tar distillers have been satisfied with selling their products in a half finished state, that is they have, with few exceptions, only isolated a few chemical compounds such as bezol, toluol, naphthalene in a pure or almost pure form. The great demand for unrefined coal-tar products for cheap roofing materials and also for the building of railroads where some of these products are used, as for instance for the impregnation of ties, poles, etc., can also partly explain our dependency on Europe for the crude materials necessary to create the industry of the manufacture of synthetic organic products and intermediate products.

It should not be inferred or taken for granted that the logical way for a country to build up the industry of artificial dyes would be to start at the bottom, that is by producing the various distillation products of coal tar, then undertaking the manufacture of the intermediate products and finally of the dyes. On the contrary the best way in many instances is just the opposite, that is, to start by producing the more complex products and to depend on the outside for the crude materials. Of course this procedure can only be carried out with co-operation of the government, that is, with protective duties, which in time can be reduced and eventually taken off altogether. This has been the line followed wherever possible by manufacturers of organic products of this country and it can readily be understood that in this manner a demand is created for the intermediate and primary products and thereby the way is paved for the further development of the manufacture of these intermediate and primary products.

In order to demonstrate the advantages to industry resulting from the application of well advised protection by duties imposed on imports, I will cite an example which I have had occasion to follow up. Chloral hydrate, a medicinal product, was manufactured many years ago in this country. Owing to the determined efforts of European firms to control this product and more especially owing to their advantage in having at their disposal cheap alcohol, the American manufacturer was obliged to discontinue the manufacture of this article.

A few years later the United States Government decided to follow the example set by most European countries in allowing the use of denatured alcohol free of tax for industrial purposes. This induced a St. Louis concern to take up the manufacture of chloral hydrate, as this was made possible by a rather high duty imposed on imported goods. The main difficulty lay in obtaining cheap chlorine. Chlorine produced

from manganese dioxide and muriatic acid or from chlorinated lime is not cheap, and for other reasons also was not satisfactory. It was hardly worth while to install an electrolytic cell as the amount of chlorine used would hardly have made it profitable, and furthermore, the caustic soda produced by the cell would have to be concentrated, which again would mean the expenditure of money for installations, which with the uncertain tariff conditions would not justify. Finally it was decided that the most convenient source of chlorine would be liquid chlorine which in Germany is obtainable at about one cent a pound, and which can be shipped in tank cars. There was, however, at that time no manufacturer of liquid chlorine in this country. The question was taken up with a firm which produces chlorine by electrolysis, and finally this firm agreed to study the question, and consequently sent some one to Europe to study the apparatus and methods used to compress chlorine to liquid chlorine which then could be shipped.

A few months later a chlorine compressor was installed, and after overcoming some difficulties this firm was able to ship liquid chlorine. Very soon new uses for liquid chlorine were found, and it began to be used in the mining industries. Later it was also found that in order to destroy the germs in the water supplied to cities liquid chlorine offered some advantages over chlorinated lime, and thereby liquid chlorine began to be used by many water works. In this manner the protection given to the manufacturer of chloral hydrate was the cause of the development of a new industry to this country. This example is by no means exceptional. I know of many other similar cases where one industry created another one, and as a matter of fact this is the history of the whole chemical industry.

The manufacturers of artificial dyes in this country depend to a great extent on Europe for crude materials, and nevertheless this industry has made remarkable advances. The textile and other industries in the United States have been steadily increasing their consumption of synthetic dyestuffs, but during the last fifteen years the large increase has been supplied from enlarged works of this country, the value of whose output was \$7,350,000 in 1899, \$10,912,000 in 1904 and \$16,428,000 in 1909, which was about 30 per cent of the domestic demand.

If not brought to an early close the effect of the present war on the manufacture in this country of synthetic organic products will undoubtedly be very great. There naturally will be financial losses owing to the inability of this industry to help itself and find substitutes in time for the many products which are now imported. Should the war last one year or even less, a great many plants will be obliged to discontinue the manufacture of certain articles. On the other hand, many new questions and also problems which have been studied before, but which now by reason of

the war have become more important, will be taken up again, and as necessity is the mother of invention, ways and means will be found to overcome many difficulties so that we can feel assured that by the time the war is over we will be wiser than we are today and will naturally derive the benefits of being wise, although we may at that time be poorer. We have already heard that, for instance, the manufacture of pure phenol has been started, and very likely has come to stay. Many of us know of other products the manufacture of which is now contemplated; in other words, the beneficial results which may derive to American chemical industries from the present war in Europe will be more noticeable in a year or two, when plans for carrying out improvements and extensions have been developed, and the depression caused by the war will have been partly relieved; for the present we have to be ready to face a siege of comparatively hard times.

I dwelt rather at length on the effect of the tariff on the development of the American chemical industry, and more particularly on the manufacture of synthetic organic products. My reason for emphasizing the tariff question is, as you probably will have understood, because I believe that the tariff is far more important to our industries than the war, and furthermore, the United States can control the making of a new tariff, whereas the United States cannot put a stop to the war at this time. My conclusion is, therefore, let us not hope to derive great advantages to our industries from this war, but let us rather make up our minds that what we need is a tariff prepared by experts uninfluenced by political pull.

I wish to quote Mr. Kerr's advice to engineers when a difficulty is encountered, an advice which is quite appropriate under the present conditions:

"Let us go as far as we can see, and then see how far we can go."

The United States Geological Survey has just printed a large, colored wall map showing the petroleum resources and the natural gas deposits of the United States, and also the thousands of miles of trunk oil pipe lines. The map shows the areas underlain by known oil pools and known gas pools, as well as general localities which are productive in either oil or gas, and also areas where there are noteworthy occurrences of either oil or gas but where there is no present production. The map is 49 by 76 inches, printed on the scale of 40 miles to 1 inch, in 5 colors. It is printed in two sheets and is sold, unmounted, by the Geological Survey, Washington, D. C., at \$1 a copy. This map not only shows graphically the oil fields and pipe lines, but is an excellent general map of the United States.

BY-PRODUCTS OF CHEMICAL PULP MANUFACTURE.*

The recovery of turpentine and rosin from woods that have been treated by chemical methods for the production of cellulose is a subject that appears to be especially attractive to manufacturers in European countries where the supply of naval stores is less abundant than in America. In the convention number of the Berlin *Papier-fabrikant* Dr. A. Luttringer is the author of an article on turpentine bodies as by-products in the manufacture of chemical pulp, of which the following is an abstract:

Timber more or less free from rosin has heretofore been preferred in the manufacture of chemical pulp. In the alkali process rosin is less troublesome than in the sulphate process and in recent years it has been possible to do away with some of the disagreeable features of the alkali process. In deciding whether the sulphite process or the soda or sulphate process is to be adopted an important point in favor of the alkali process must be considered in future, namely, the possibility of obtaining turpentine bodies as by-products. On the other hand some manufacturers who formerly extracted resinous substances from the timber found it profitable to make the resulting residues of wood into chemical pulp. Only recently has the advance been made of manufacturing chemical pulp and obtaining rosins in one operation.

In order to make the recovery of turpentine, etc., a profitable undertaking the timber must be fairly rich in rosin. By the term rich in rosin the manufacturer of chemical pulp understands something different from that understood by the manufacturer of rosin products. The latter goes much further in this direction, since the extraction of the resinous substances necessitates an expenditure which must at least be covered by the sale of the products obtained.

The first attempt to obtain turpentine as a by-product in the manufacture of soda cellulose was made in 1875 by Dr. M. Faudel at the chemical pulp mill at Danzig. The horizontal digesters having a steam dome are particularly suitable for the purpose. As is well known, turpentine can be distilled over in a current of steam at 100° C. When, however, the timber is in the form of chips of the normal size the entire turpentine contained in the wood does not pass over. Probably a part of the turpentine must first be liberated by the alkaline treatment.

Turpentine obtained in the manufacture of sulphate pulp is unfit for use owing to the evil-smelling substances produced in the sulphate process. Bergström and Fagerlind found in such a turpentine methyl sulphide to the extent of 30 per cent, and this, as is well known, is a solvent of nitrocellulose. By nitric oxidation there is formed from the methyl sulphide an oxygen derivative which boils at 200° C. and is also a solvent of nitrocellulose. Perhaps this will result in a

profitable employment of the impurities contained in sulphate turpentine.

The yield of turpentine fluctuates according to the proportion of rosin contained in the wood. According to Kirchner 1 cubic meter of timber yields 0.8 to 5 kilos of crude turpentine. According to Schwalbe fir yields 1.5 kilos crude turpentine per 1,000 kilos chemical pulp, or 1 kilo rectified turpentine.

Pine may yield up to 11 kilos of crude turpentine, including 2 kilos of methyl sulphide. Klason found a yield of turpentine per 1,000 kilos of timber of 0.4 kilo for fir and 5 kilos for pine.

The turpentine obtained in the soda process is mostly fit for immediate sale, while that obtained in the sulphate process must first be purified. For purifying the turpentine various proposals have been made, as follows:

- (1) Leave it standing in the air (disadvantage; loss of turpentine).
- (2) Distillation (Klason doubts the utility of this process, proposed by Bergström and Fagerlind).
- (3) Stirring in the sun, if necessary, with admixture of chloride of lime (Knösel).
- (4) Treatment with about 50 per cent sulphuric acid (Klason considers this impracticable with impure or too old turpentine).
- (5) Treatment with gaseous nitrogen oxides (Schwalbe).

The solid rosin contained in the wood can also be obtained in a more or less perfect manner.

G. Schacht has proposed to employ the waste water for sizing packing paper.

If the evaporation of the wash is stopped at a certain point an oil layer consisting of soda salts of rosin bodies and of high fatty acids floats on the surface. This oil is known on the market as pine oil or liquid rosin. Its price is somewhat low and it is used for sizing common papers or for making rosin oils.

According to Bergström the liquid rosin yields a dark brown solution with hot water. When acid is added a gray mass is precipitated which on being heated is converted into a thick oil. Liquid rosin contains colophony acids, palmitic acids and also very probably oleic acid and linoleic acid. In the wood itself the fatty acids are probably chemically combined with glycerin. Lastly, liquid rosin contains phytosterin, whether it comes from pine or from fir.

As already mentioned, all the processes are carried out in two parts, viz.: extraction of the rosin; conversion of the residue into chemical pulp, mostly according to one of the well known processes.

The processes that appear best from a theoretical standpoint consist in extracting the rosins by organic solvents, *e. g.*, a mixture of alcohol and gasoline, or ether, or gasoline with carbon bisulphide, or with solvents which form an emulsion with water at a high temperature, or with heavy hydrocarbons of a high

*From Paper.

boiling point, etc. In practice these organic solvents have not been used, presumably owing to the unavoidable losses by leakage from the apparatus.

In most of the processes mentioned the same reagent is employed for the extraction of the rosin and for digesting the cellulose. The advantages of performing the two operations in one were early recognized. The solution of the problem was not easy, however, and only recently has success been obtained in this direction. Attention may be directed to the interesting laboratory experiments by F. P. Veitch. We have already reported in this journal the details of the process protected in France by the patent 463,879, dated December 28, 1912. In this process the turpentine is collected at the beginning of the cooking, the solid rosin is emulsified, the emulsion is evaporated and incinerated. Besides the soda residues which are employed again in known manner a distillate is obtained which can be decomposed by suitable treatment into rosin oils, reten, phenols, methyl alcohol, etc.

In a later issue of the *Papierfabrikant* the article by Dr. Luttringer is supplemented by the following:

Pure oil of turpentine to the extent of five kilos (11 lb.) per ton of chemical pulp can be obtained from the waste wash of sulphate pulp mills which use 70 per cent pine and 30 per cent spruce, and an additional amount can be recovered from the condensate of the digesters. The residue consists principally of methyl sulphide.

At the present time methyl sulphide is not used at all in the arts. The author has had personal experience of the narcotic action of this substance and deems it advisable to investigate methyl sulphide in this respect. The most advantageous method of purifying crude sulphate turpentine oil is that of Bergström-Fagerlind. The crude turpentine is first carefully subjected to fractional distillation. Methyl mercaptan, methyl sulphide and methyl disulphide, all of which boil more readily than the terpenes, escape. For the removal of ammonia, amines and amides treatment with sulphuric acid should follow.

Old oxidized sulphate turpentine must always have the rosin removed from it by distillation before being treated with sulphuric acid. The liquid rosin is used for sizing paper and for making rosin-oil grease. Refined pine oil can be used in making soaps, putty and probably also in the manufacture of varnish. The pitch is used as insulating material in the manufacture of cables.

In most cases the manufacture of pine oil is not likely to be profitable at the present price.

POTASH DEPOSITS IN SPAIN.*

Fully 25 years ago a Spanish mining engineer called the attention of the Spanish Government to the importance of making investigations in certain provinces of Catalonia in order to locate deposits of potassium salts that he believed to exist in that part of Spain. No particular investigation, however, was undertaken, although it was generally understood that potash existed in some quantity in the northeastern parts of Spain, of which Barcelona is the chief city.

Within the past three or four years important deposits of potassium salts were found in shafts sunk in construction work in salt mining near Suria, south of Cardona, for which that neighborhood has long been famous. When this discovery became known some important foreign companies, with the help of Spanish interests, sought for many extensive mining concessions, both near Suria and in many other localities where there was any geological indication that potash might possibly exist. Up to August 1, 1914, borings were being made in various parts of the territory in question by one or another of the interested companies in order to determine the exact chances of exploiting potash mines. Even in view of negative results, it was of paramount importance for foreign companies to know exactly where the potash monopoly would remain.

Up to the present potash has not been extracted in Spain in commercial quantities. It has been proved, however, that potash does exist near Barcelona, that it is fairly amenable to refining, and that the deposits may become a basis of a world trade, with Barcelona as an export center. Examination and tests thus far have indicated only enough potash for consumption in Spain, but they have been so limited that it is impossible to estimate the quantity and grade of the deposits and the difficulties that may have to be undertaken in mining for this salt.

It is presumed from the varied data gathered that the potash beds are extensive and rich and likely to have an important bearing on agriculture and certain highly important manufacturing industries, both in the peninsula and abroad. What is now needed is a scientific and extensive survey of the regions in this part of Spain where marked traces of potassium salts have been found. For local consumption it is now probably possible to put certain quantities of potash on the market. As an article for export in regular and unfailing shipments present indications do not point to a definite or even early conclusion.

The tracts in Catalonia in which beds of potassium salts exist are chiefly in the two provinces of Barcelona and Lerida, particularly in the latter near the towns of Suria and Cardona on the Cardoner River. At present, concessions do not go beyond Solsona on the north and the towns of Tarrega, Servera, and

*From Daily Consular and Trade Reports.

According to L'Économiste Européen the production of gold in Rhodesia during the first six months of 1914 was valued at \$8,149,178, compared with \$6,872,325 during the corresponding period of 1913.

Manresa on the south, the entire district being practically confined between the Segre and Llobregat Rivers. In this delimited region a number of these claims for mining concessions has been made on lands where there is no conclusive proof that potash exists in commercial quantities, although it is possible that these lands contain potash and that the potash-producing area may extend considerably beyond the confines mentioned. Thus far the prospecting has been satisfactory at and near Suria, but a thorough investigation must be made at Cardona and Callús, nearly midway between which Suria is situated.

The potash now used in Spain must be imported at prices over which the buyer has no control. Consumers of potash in Spain are urged to free themselves of this dependence. It is thought that Spanish potash can be put on the market at much lower figures than those now quoted for the imported article. The consumption is growing rapidly in Spain, where the potash is extensively used in the olive groves, vineyards, and wheat fields.

There will be some difficulty in arriving at an accurate estimate as to the extent of the potash beds, because the salt does not lie in a regular basin, as in upper Alsace and at Strassfurt, Germany. Borings will have to be made with expert knowledge of the geological formation of the country under consideration. A Spanish mining engineer has stated that an appreciable amount of capital will be required to make the necessary survey in Catalonia, but that the chances for finding potash in remunerative quantity are favorable.

In July, 1914, a bill was presented in the Cortes by the Minister of Public Works for the purpose of submitting to state intervention the exploitation of potassium salts and other minerals of great national importance. The bill, which has not yet become law, provides that uninterrupted working of concessions be granted, whether for carrying on experimental boring or for exploiting potash itself. The state will be empowered to subordinate the exploitation to the interests of the country and impose special conditions in favor of the consumption in Spain, independently of the financial measures that may be adopted relative to exportation. A mine that produces potash may not suspend its operations as long as the potash is minable, except for the following reasons: On account of an accident or force majeure; through a possible crisis which affects the consuming markets and the minerals produced in the mine; or when the net value of the products extracted does not cover the cost of production of the same. The state may reserve to itself the right of concession to mineral-producing lands that may be brought to its attention by its official experts.

A royal decree published October 1, 1914, directs that the state may reserve the right to exclude either temporarily or definitely concessions for free lands;

that the Ministry of Public Works may designate for the purpose of investigating, discovering, or, if seen fit, using such lands as may be productive of marketable mineral substances used as agricultural fertilizers or as materials that can be employed in the manufacture of the same. The Geological Institute of Spain will designate the lands or zones which should be reserved or investigated. This work will be carried out by the proper technical departments of the Spanish Government. The reservation of such lands in favor of the state will be of three kinds: Provisional, for preliminary study; temporary, for thorough investigation; definite, for exploitation. If the investigations carried out by the Geological Institute result in the discovery of mineral wealth, or indicate its existence, the rights to such land as is productive thereof having been temporarily reserved will be vested in the state.

Furthermore, the state may preempt, lease, or exploit on its own account the deposits that it reserves, in conformance with the mining laws or such other laws as may be hereafter enacted. The mining engineers belonging to any of the auxiliary investigating bureaus or departments who have been instrumental in locating mineral deposits, such as indicated and which the state reserves definitely, will have the right to a special reward in proportion to the value of the deposits discovered. These rewards will be adjusted according to the following scale: 1 per cent for a valuation less than 1,000,000 pesetas (\$180,000); three-fourths of 1 per cent for a valuation from 1,000,000 pesetas (\$180,000) to 5,000,000 pesetas (\$900,000), both inclusive; one-half of 1 per cent for a valuation above 5,000,000 pesetas (\$900,000).

The state now reserves temporarily the right to the lands in the Provinces of Barcelona and Lerida concerning which the Geological Institute has made investigations as to potassium salts, and which from now on will be reserved and excluded temporarily from the right of private preemption, and also of all the lands embraced within the perimeter indicated by the towns of Balaguer, Tarrega, Igualada, Manresa, Vich, Berga, and Isona.

Moreover, the right to exploit potash will be suspended in case it is found in lands that have been preempted for other classes of minerals. The Geological Institute is enjoined to proceed immediately with a detailed study of the territory mentioned in the reserved perimeter, submitting to the Spanish Government the plan and estimate appropriate for the investigation in question and render an official report of its labors and operations.

Aside from the comparatively small quantities produced by its African colonies, Germany, like other industrial Europe, is dependent upon the imports of cotton from other countries. The industries of Germany consumed annually 1,000,000,000 lbs. of cotton, of which four-fifths come from the United States.



METHODS OF ANALYSIS USED IN THE LABORATORIES OF THE ARMOUR INSTITUTE OF TECHNOLOGY.

Analysis of Fertilizers and Fertilizer Materials.

There are many different materials used as fertilizers, the essential requirements being that they contain compounds of potassium, phosphorus or nitrogen in such a form that they will be available for plant food, and that they can be obtained at a price which will enable them to be used as fertilizers.

Notwithstanding the diversity of materials which we may find on the market as fertilizers the number of determinations necessary for their proper valuation is not very extensive.

The determinations commonly made are potassium, reported as K_2O ; total phosphorus, reported as total P_2O_5 ; water soluble phosphorus, reported as water soluble P_2O_5 ; citrate insoluble phosphorus, reported as citrate insoluble P_2O_5 ; total nitrogen, which includes all compounds of nitrogen, nitrates, nitric and ammoniacal nitrogen, moisture; and in some fertilizing materials such as "stick," tankage, garbage and garbage tankage, grease is usually determined.

Preparation of the Sample.—Some of these fertilizer materials reach the chemist in the proper shape to be sampled and analyzed directly. There are other materials which require some preparation on the part of the chemist before they can be sampled for analysis. A short description will be given of the methods applicable to certain of these materials. Tankage, garbage and garbage tankage should first be prepared as air-dried samples. This is best done by weighing out a considerable quantity of the material ranging from two to five pounds, depending on whether the material is rather homogeneous or not. This sample is ground in an ordinary food chopper. The entire weighed sample is placed in a shallow pan in the drying closet until the sample reaches a nearly dry condition. It is then weighed and the loss of weight noted. This partially dried sample is then ground to pass a sieve with 1mm. openings and this finer ground sample is used for the final determination of moisture and other fertilizer constituents while the thoroughly dried sample from the moisture determination is used for the determination of grease.

Sample of "stick" received in the laboratory are weighed out into shallow pans or trays usually in quantities of $1\frac{1}{2}$ to 2 pounds and dried in the vacuum oven. During the process of drying, the material is usually taken out a few times and stirred or scraped up from the pan so that drying will proceed rapidly

and completely. The sample obtained in this way is ground and the dry ground material is used for the determination of grease and for the determination of the fertilizer constituents.

This sample is quite hygroscopic and must be kept in such a way that all moisture is excluded.

The grease in these samples is determined by weighing out a 2 gram sample of the properly prepared dry material, placing it in a Schleicher and Schull fat-free capsule and extracting in a Soxhlet extractor for four hours using pure carbon disulphide as the extracting agent. Ether may be used as the extracting agent, but in case it is more care is necessary in preparing the dried sample and in seeing that the ether itself is thoroughly free from moisture.

The determinations which are common to fertilizer materials follows:

Total Phosphorus.—Weigh out 2 grams of the sample and dissolve by treating with 30 cc. of con. nitric acid and about 5 cc. of hydrochloric acid. Boil until all organic matter is destroyed and then evaporate almost to dryness. Add 25 cc. con. nitric acid and boil for 30 minutes.

The solution made as described above is placed in a 250 cc. flask and made up to volume.

Determination.—Take an aliquot portion of the solution prepared as directed and which is estimated to correspond to .25, .50 or 1 gram of the original material, depending on the quantity of phosphorus supposed to be present in the sample. Neutralize with ammonium hydroxide, and then make acid with a small quantity of nitric acid. Heat the solution to a temperature of approximately $80^\circ C$. and add 50 cc. of molybdate solution for every decigram of P_2O_5 that is supposed to be present. Digest at about $65^\circ C$. for an hour; filter, and wash with 1 per cent ammonium nitrate solution. When the washings are free from acid dissolve the precipitate in a standard sodium hydroxide solution containing 323.81 cc. of normal sodium hydroxide in one liter; 10 cc. of this solution should neutralize 3.24 cc. of normal acid and 1 cc. will equal 1 milligram of P_2O_5 . When the phosphorus precipitate has all gone into solution in the standard sodium hydroxide solution, phenolphthalein is added as indicator and the excess of sodium hydroxide is determined by titration with standard acid. The acid should be made so that 1 cc. of it is just equivalent to 1 cc. of the standard sodium hydroxide solution.

Water-soluble Phosphoric Acid.—Place 2 grams of the sample on a 9-cm. filter, wash with successive small portions of water, allowing each portion to pass

through before adding more, until the filtrate measures about 250 cc. If the filtrate be turbid, add a little nitric acid. Make up to any convenient definite volume, mix well, use an aliquot, and proceed as under total phosphoric acid.

Citrate-insoluble Phosphoric Acid.—(a) Determination in acidulated samples: Heat 100 cc. of strictly neutral ammonium citrate solution of 1.09 specific gravity to 65° C. in a flask placed in a warm-water bath, keeping the flask loosely stoppered to prevent evaporation. When the citrate solution in the flask has reached 65° C. drop into it the filter containing the washed residue from the water-soluble phosphoric acid determination, close tightly with a smooth rubber stopper, and shake violently until the filter paper is reduced to a pulp. Place the flask in a bath and maintain it at such a temperature that the contents of the flask will stand at exactly 65° C. Shake the flask every five minutes. At the expiration of exactly thirty minutes from the time the filter and residue are introduced remove the flask from the bath and immediately filter the contents as rapidly as possible. Wash thoroughly with water at 65° C. (1) Transfer the filter and its contents to a crucible, ignite until all organic matter is destroyed, add from 10 to 15 cc. of strong hydrochloric acid, and digest until all phosphate is dissolved; or (2) return the filter with contents to digestion flask, add from 30 to 35 cc. strong nitric acid, from 5 to 10 cc. strong hydrochloric acid, and boil until all phosphate is dissolved. Dilute the solution to 200 cc. Mix well, filter through a dry filter; take a definite portion of the filtrate and proceed as under total phosphoric acid.

(b) Determination in nonacidulated samples: In case a determination of citrate-insoluble phosphoric acid is required in nonacidulated samples it is to be made by treating 2 grams of the phosphatic material without previous washing with water, precisely in the way above described, except that in case the substance contains much animal matter (bone, fish, etc.), the residue insoluble in ammonium citrate is to be treated by the processes described under total phosphoric acid.

Total Nitrogen.—Determination: Place from 0.7 to 3.5 grams of the substance to be analyzed in a Kjeldahl digestion flask, add 30 cc. of sulphuric acid containing 1 gram of salicylic acid and shake until thoroughly mixed, then add 5 grams of crystallized sodium thiosulphate, shaking the contents of the flask at the same time. Finally, place the flask on the stand for holding the digestion flasks, where it is heated over a low flame until all danger of frothing has passed. The heat is then raised until the acid boils briskly and the boiling continued until white fumes no longer escape from the flask. This requires about five or ten minutes. Add approximately 0.7 of a gram of mercuric oxide, or its equivalent in metallic mercury, and 10 grams of potassium sulphate, and continue the boiling until the liquid in the flask is colorless. In case the contents of the flask are likely to become solid before

this point is reached, add 10 cc. more of sulphuric acid.

After cooling dilute with about 200 cc. of water, add a few pieces of granulated zinc or pumice stone when this is necessary in order to keep the contents of the flask from bumping, and 25 cc. of potassium sulphide solution with shaking. Next add 50 cc. of the soda solution, or sufficient to make the reaction strongly alkaline, pouring it down the side of the flask so that it does not mix at once with the acid solution. Connect the flask with the condenser, mix the contents by shaking, and distill until all ammonia has passed over into the standard acid. The first 150 cc. of the distillate will generally contain all the ammonia. This operation usually requires from forty minutes to one hour and a half. The distillate is then titrated with standard alkali.

The reagents required for this determination are as follows:

Standard acid solution: Standard hydrochloric acid, the absolute strength of which has been determined by precipitating with silver nitrate and weighing the silver chloride as follows:

By means of a preliminary test with silver nitrate solution, to be measured from a burette, with excess of calcium carbonate to neutralize free acid and potassium chromate as indicator, determine exactly the amount of nitrate required to precipitate all the hydrochloric acid. To a measured, and also to a weighed portion of the standard acid add from a burette one drop more of silver nitrate solution than is required to precipitate the hydrochloric acid. Heat to boiling, cover from the light, and allow to stand until the precipitate is granular. Then wash with hot water through a Gooch crucible, testing the filtrate to prove excess of silver nitrate. Dry the silver chloride at 140° to 150° C.

Standard alkali solution: The strength of this solution relative to the acid must be accurately determined; tenth-normal solution is recommended.

Sulphuric acid: The sulphuric acid used should have a specific gravity of 1.84 and be free from nitrates and also from ammonium sulphate.

Metallic mercury, or mercuric oxide: If mercuric oxide is used, it should be prepared in the wet way, but not mercuric nitrate.

Granulated zinc or pumice stone: One of these reagents is added to the contents of the distillation flasks, when found necessary, in order to prevent bumping.

Potassium sulphide solution: A solution of 40 grams of commercial potassium sulphide in 1 liter of water.

Sodium hydroxide solution: A saturated solution of sodium hydroxide free from nitrates.

Indicator: A solution of cochineal is prepared by digesting and frequently agitating 3 grams of pulverized cochineal in a mixture of 50 cc. of strong alcohol and 200 cc. of distilled water for a day or two at ordinary temperatures. The filtered solution is employed as indicator.

The apparatus used in determination is as follows:

Kjeldahl Flasks for both Digestion and Distillation: These are flasks having a total capacity of about 550 cc. made of hard, moderately thick and well annealed glass. When used for distillation the flasks are fitted with rubber stoppers and bulb tubes, as given under distillation flasks.

Kjeldahl Digestion Flasks: These are pear-shape, round bottom flasks, made of hard, moderately thick, well annealed glass, having a total capacity of about 250 cc. They are 22 cm. long and have a maximum diameter of 6 cm., tapering gradually to a long neck, which is 2 cm. in diameter at the narrowest part and flared a little at the edge.

Distillation Flasks: For distillation, a flask of ordinary shape of about 550 cc. capacity may be used. It is fitted with a rubber stopper and with a Hopkins bulb tube above to prevent the possibility of sodium hydrate being carried over mechanically during distillation. The bulbs may be about 3 cm. in diameter, the tubes being of the same diameter as the condenser and cut off obliquely at the lower end, which is fastened to the condenser by a rubber tube.

Ulsch Method, Modified by Street.—(Applicable to all nitric and ammoniacal nitrogen determinations.) Place one gram of the sample in a half liter flask. Add about 30 cc. of water and 2 to 3 grams of reduced iron, and after standing sufficiently long to insure solution of the soluble nitrates and ammonia salts add 10 cc. of a mixture of strong sulphuric acid with an equal volume of water; shake thoroughly and allow to stand for a short time until the violence of the reaction has moderated. Place a long stemmed funnel in the neck of the flask to prevent mechanical loss. Heat the solution slowly, boiling it for five minutes and cool. Add about 100 cc. of water, a little paraffin, and from 7 to 10 grams of magnesium oxide, free or nearly free from carbonates. Connect with a condenser such as is used in the Kjeldahl method, and boil the mixture for 40 minutes, nearly to dryness; collect the ammonia in a known amount of standard acid, and titrate in the usual manner. The nitrogen obtained represents the nitrates, plus the ammonia salts, contained in the sample.

In the analysis of nitrate salts proceed as above, except that 25 cc. of the nitrate solution, equivalent to 0.25 gram of sample, are employed with 5 grams of reduced iron. After boiling add 75 cc. of water and an excess of sodium hydrate and complete the determination as above.

Alkaline-Permanganate Method. (For the determination of available organic nitrogen): Weigh out an amount of sample containing 0.045 gram of nitrogen and transfer to a 600 cc. distillation flask. After connecting with a condenser, to which a receiver containing standard acid has been attached, digest below the boiling point with 100 cc. of alkaline permanganate solution (16 grams of potassium permanganate and 150 grams of sodium hydroxide dissolved in water and made to volume of 1 liter), for thirty minutes. Then

boil until 85 cc. of the distillate is obtained. If the material shows a tendency to adhere to the sides of the flask, an occasional gentle rotation is necessary during distillation.

Potassium.—Lindo-Gladding Method.

Preparation of Reagents—Ammonium Chloride Solution: Dissolve 100 grams of ammonium chloride in 500 cc. of water, add from 5 to 10 grams of pulverized potassium-platinic chloride and shake at intervals for six or eight hours. Allow the mixture to settle over night and filter. The residue may be used for the preparation of a fresh supply.

Platinum Solution: The platinum solution used contains one gram of metallic platinum (2.1 grams of H_2PtCl_6) in every 10 cc.

Methods of Making Solution—With Potash Salts and Mixed Fertilizers: Boil 10 grams of the sample with 300 cc. of water for 30 minutes. In the case of mixed fertilizers, add to the hot solution a slight excess of ammonium hydroxide and then sufficient powdered ammonium oxalate to precipitate all the lime present. Cool, dilute to 500 cc., mix, and pass through a dry filter. In the case of muriate and sulphate of potash, sulphate of potash and magnesia and kainit, dissolve and dilute to 500 cc. without the addition of ammonium hydroxide and ammonium oxalate.

With Organic Compounds: When it is desired to determine the total amount of potash in organic substances, such as cottonseed meal, tobacco stems, etc., saturate 10 grams with strong sulphuric acid, and ignite in a muffle at a low red heat to destroy organic matter. Add a little strong hydrochloric acid, warm slightly in order to loosen the mass from the dish, and proceed as directed in the determination below.

Determination—In mixed Fertilizers: Evaporate 50 cc. of the solution corresponding to 1 gram of the sample, nearly to dryness, add 1 cc. of dilute sulphuric acid (1 to 1), evaporate to dryness, and ignite to whiteness. As all the potash is in the form of sulphate, no loss need be apprehended by volatilization of potash, and a full red heat must be maintained until the residue is perfectly white. Dissolve the residue in hot water, using at least 20 cc. for each decigram of potassium oxide, add a few drops of hydrochloric acid, and platinum solution in excess. Evaporate on a water bath to a thick paste and treat the residue with 80 per cent alcohol, sp. gr. 0.8645 avoiding the absorption of ammonia. Wash the precipitate thoroughly with 80 per cent alcohol both by decantation and on the filter continuing the washing after the filtrate is colorless. Wash finally with 10 cc. of the ammonium chloride solution to remove impurities from the precipitate and repeat this washing five or six times. Wash again thoroughly with 80 per cent alcohol and dry the precipitate for 30 minutes at 100° C. The precipitate should be perfectly soluble in water.

Muriate of Potash: Dilute 25 cc. of the solution, prepared as described under "Methods of Making So-

lution with Potash Salts and Mixed Fertilizers" with 25 cc. of water, acidify with a few drops of hydrochloric acid, add 10 cc. of platinum solution and evaporate to thick paste. Treat the residue as in determination in mixed fertilizers.

Sulphate of Potash—Sulphate of Potash and Magnesia, and Kainit: Dilute 25 cc. of the solution prepared as under Muriate of Potash Determination with 25 cc. of water, acidify with a few drops of hydrochloric acid and 15 cc. of platinum solution. Evaporate the mixture and proceed as directed in determination in mixed fertilizers except that 25 cc. portions of ammonium chloride solution should be used.

Water-soluble Potash in Wood Ashes and Cotton Hull Ashes: Use the above method, making solution in like manner and paying special attention to the fact that precipitate should be perfectly soluble in water.

THE CHEMICAL ANALYSIS OF PAPER.*

By HENRY ALDOUS BROMLEY.

The materials entering into the composition of paper in its finished state may be classified as follows: (1) Fibrous foundation; (2) moisture; (3) mineral matter; (4) sizing materials; (5) coloring matters; (6) substances added for special purposes; (7) chemical residues, etc. Such of the foregoing as admit of quantitative estimation by chemical means are considered in this article.

The two fibrous materials admitting of quantitative estimation with any degree of accuracy are: (1) Esparto and (2) mechanical woodpulp.

This process depends on the fact that the acid distillation of an oxycellulose yields furfuraldehyde in direct relation to the amount of fiber present in the paper. The determination is conducted as follows: A flask is prepared through the cork of which passes a stoppered separating funnel and having a glass outlet tube connected with a Liebig's condenser. In the flask is placed 5 gm. of the paper to be examined, cut into small pieces, and 100 cc. of hydrochloric acid of specific gravity 1.06. The flask is then heated in such a manner that 2 cc. of distillate per minute are delivered, a graduated measure being used for its collection. When the distillate reaches 30 to 40 cc. it is removed to a flask, and two or three further portions collected in the same way. As each portion of distillate is removed from the collecting measure a corresponding further amount of hydrochloric acid is added to the distilling flask. The distillation is continued until a drop of the distillate ceases to give the aldehyde reaction with aniline acetate.

This reaction is obtained by allowing a drop of the last portion of distillate to fall from a glass rod into a solution of aniline acetate acidified with acetic acid in a white hasin. In the presence of an aldehyde a rose red coloration is produced. Failure of the dis-

tillate to give the reaction shows that the distillation is complete. The separate portions of distillate are mixed together in a beaker, and the hydrochloric acid present neutralized with a slight excess of sodium carbonate, after which a small quantity of acetic acid is added.

For the precipitation of the furfural a solution is prepared containing 12 gm. of phenylhydrazine and 7.5 gm. of glacial acetic acid in 100 cc. distilled water. This solution is added to the distillate until a drop of the latter ceases to give the aldehyde reaction previously described. The solution is set aside for some hours with occasional stirring for the golden crystalline precipitate of furfural hydrazone formed to separate out, which it does according to the following equation: $C_5H_4O_2 + C_6H_5N_2H_3 = C_5H_4ON_2HC_6H_5 + H_2O$.

The precipitate after being washed is filtered off through a weighed Gooch crucible. The crucible and its contents are dried in a current of air at about 60° C. and weighed. The weight of precipitate multiplied by .538 gives the weight of furfural. The average yield of furfural from 100 parts of esparto has been shown to be 12.5. The weight of esparto present in the 5 gm. of paper is therefore obtained by multiplying the weight of furfural by 8, whence the percentage weight is easily calculated.

Several methods have been suggested for the determination of groundwood in paper. The best known is probably that of Würster, which depends on the depth of color produced with di-methyl-paraphenylenediamine. Paper impregnated with this substance can be obtained, together with a scale of colors corresponding to the tints produced by various percentages of mechanical wood. The test paper is moistened and laid between a fold of the paper to be tested. In the presence of mechanical wood the paper is colored red and the tint is then compared with the standard color scale.

The method of Godeffroy and Coulon depends on the property of lignin of reducing a solution of gold chloride to metallic gold. For the estimation a weighed quantity of paper is torn into small pieces and divided into two portions of equal weight. Each portion is boiled for ten minutes in a 10-per cent solution of ammonia washed, and dried. One portion is now burned and the ash determined. The second portion is treated by boiling with a solution of tartaric acid, followed by extraction with alcohol and ether to remove the size, and is then boiled for a further ten minutes with a 10-per cent solution of gold chloride, being afterwards washed, dried, and finally ashed. On deducting the weight of the ash obtained in the first determination from that obtained in the second, the amount of reduced gold is found. This amount is a measure of the lignone groups present and, therefore, of the amount of mechanical wood. The weight of gold multiplied by 4.7 (the average factor obtained from a number of

*From The Paper-Maker and British Paper Trade Journal

determinations) gives the weight of mechanical wood in the amount of paper taken for analysis.

In the phloroglucin method of Cross, Bevan, and Briggs advantage is taken of the power of ligneous tissue to absorb a solution of standard phloroglucin, the amount of absorption being directly related to the quantity of mechanical wood present. The estimation is carried out as follows: Two grammes of the paper are pulped, dried at 100° C. and weighed. The weighed pulp is transferred to a dry flask, covered with 40 cc. of a solution made by dissolving 2.5 gm. of pure phloroglucin in 500 cc. of hydrochloric acid of specific gravity 1.06 shaken, and allowed to stand for some hours. The liquid is then filtered through cotton placed in the neck of a funnel, and 10 cc. of the filtrate taken for titration. This 10 cc. is mixed with 20 cc. of hydrochloric acid (specific gravity 1.06), heated to 70° C., and titrated with a standard solution of formaldehyde made by dissolving 1 cc. of 40-per cent formaldehyde solution in 500 cc. of hydrochloric acid (1.06 specific gravity). The aldehyde solution is added from a burette 1 cc. at a time with an interval of two minutes between each addition. A piece of cheap newspaper is used as an indicator, free phloroglucin producing a red stain when a drop of the liquid is allowed to fall on the paper. Toward the end of the reaction it becomes necessary to dry the paper before a bunsen burner before the stain will appear. Treated in this way one part of phloroglucin in thirty thousand gives a perceptible stain. When no further color is produced the reaction is complete; 10 cc. of the original phloroglucin solution are now titrated in the same way, the difference between the two results giving the amount absorbed by the lignin. The proportion of mechanical wood in the paper is calculated from the following formula:

$$H = 100 \frac{(p - 1.0)}{8 - 1.0}$$

Where H = per cent of mechanical wood.

p = absorption value of the dry ash-free sample.

8 = absorption value of mechanical wood.

1 = absorption value of sulphite wood.

Another method depends upon the action of chlorine gas on lignin. The paper under examination is rendered neutral by first boiling with a weak solution of sodium carbonate, treating with weak acetic acid, and then washing with hot water. It is then exposed in a damp condition to the action of chlorine gas, which enters into combination with the lignin. After the chlorination is complete the excess of chlorine is removed and a known quantity of water added, and the resulting hydrochloric acid determined by titration with standard soda. Each cc. of normal soda used is said to be equivalent to .22 gm. of mechanical wood pulp.

In practice it is usually only necessary to make a

determination of added moisture in paper. For such determination it is best to weigh a whole sheet. Dry this at 100° C. in the oven, and then allow the sheet to cool while freely exposed to the atmosphere of the laboratory. The loss of weight gives the amount of moisture over and above that normally present, and is expressed as a percentage on the weight of the sheet.

One gm. of paper is torn into fragments and incinerated in a weighed platinum crucible, tilted at an angle to allow free access of air. If difficulty is experienced in completely burning off the last charred particles the residue may be moistened with a few drops of ammonium nitrate and the heating continued. When the ash is almost completely white the crucible is cooled and weighed and the weight of ash determined by difference. The ash is expressed as a percentage on the weight of paper taken. Where this weight is 1 gm. the weight of ash gives the percentage figure directly, if the decimal point be moved two places to the right. Thus, .155 gm. = 15.5 per cent.

An alternative method consists in tearing the paper into three or four pieces, and impaling these on the free ends of a piece of twisted platinum wire let into a glass holder. The incineration process is thus somewhat accelerated.

These may be china clay, pearl hardening, blanc fixé, talc, and satin white, either separately or in admixture. Where any one loading is present alone its determination is practically identical with that of the ash, after correction for that normally due to the fibrous material of the paper. In the case of pearl hardening (calcium sulphate) and blanc fixé (barium sulphate) some reduction of the sulphate to sulphide takes place on ignition, and the ash requires moistening with sulphuric acid and reheating before its weight is determined. Loading materials contain more or less water which is driven off at a red heat, and this loss should be allowed for in the calculation. Thus pearl hardening normally contains two molecules of water (20 per cent) and china clay about 12 per cent.

Pearl hardening and satin white in admixture with other loadings are easily separated from them by reason of their ready solubility in dilute hydrochloric acid. For the determination of blanc fixé, talc, and china clay the residue after ignition is fused with several times its own weight of fusion mixture in a platinum crucible. By this means the bases are converted into carbonates, while the sulphates and silicates enter into combination with the sodium and potassium of the fusion mixture. The fused mass is treated with hot water for some time to dissolve out the soluble sulphates and silicates, after which the liquid is filtered and the filtrate set aside for determination of the acids. The insoluble residue, which may contain barium, aluminum, and magnesium carbonates, is dissolved in dilute hydrochloric acid and the solution reserved for determination of the bases.

The filtrate reserved for the determination of the acids as above is acidified with hydrochloric acid, evaporated to dryness, moistened with more hydrochloric acid, heated for a short time on the sand bath, and the residue taken up with hot water. This causes the separation of *silica* which is then filtered off, washed, dried, ignited, and weighed. The filtrate from this last operation is heated to boiling, and *sulphates*, if present, precipitated with barium chloride in the usual way, filtered, and the precipitate washed, dried, ignited, and weighed.

The solution reserved for the determination of the bases is treated with strong ammonia to precipitate *alumina*, which latter is filtered off, washed, dried, ignited, and weighed. The filtrate from this last operation is treated with ammonium sulphate to precipitate *barium*, which is then ignited and weighed as barium sulphate. The final filtrate is evaporated to small bulk half its volume of ammonia added, then excess of a solution of sodium phosphate, and any resulting precipitate estimated as magnesium pyrophosphate in the usual manner.

These bodies being nitrogenous and containing fairly constant proportions of nitrogen, their estimation resolves itself into a determination of nitrogen. The determination may be made by either of two methods, viz., by combustion with soda-lime or by Kjeldahl's process. The latter, being the simpler and more generally employed process, is the one described here. Kjeldahl's process depends on the fact that when most nitrogenous bodies are heated with excess of concentrated sulphuric acid their nitrogen is converted into ammonium sulphate, from which the nitrogen may be liberated by treatment with excess of alkali and distilling.

Into a special hard glass flask is introduced from 1 to 2 gm. (according to the probable proportion of gelatin present) of the paper torn into shreds, followed by about 20 cc. of concentrated sulphuric acid (free from nitrous compounds) and .5 gm. red mercuric oxide. The flask is supported by the neck in an inclined position and gradually heated up to nearly the boiling point of the acid. At this stage 5 gm. of potassium sulphate are added to raise the boiling point, and the heating is continued. The liquid is at first black but becomes lighter in color as the reaction goes on, passing through brown to yellow, and finally becoming almost colorless.

The reaction usually takes several hours to complete, but once started may safely be left to itself. A crystal of copper sulphate added during the later stages will hasten completion. When the nearly colorless contents of the flask are cold they are diluted with a considerable bulk of water, and transferred to a 500-cc. copper distilling flask, together with enough of a 50 per cent solution of caustic soda to render the liquid alkaline, 20 cc. of a weak solution of potassium sulphide, and one or two pieces of broken clay pipe stem

or pumice. A special, bent delivery tube arranged to act as a condenser is used, fitted into the cork of the distilling flask, the other end dipping into a graduated measure containing a known volume (about 20 cc.) of one-tenth normal sulphuric acid.

The liquid in the flask is now rapidly distilled for about half an hour, by which time all the ammonia will have come over. Care must be taken so to regulate the heat that neither the liquid in the flask tends to be driven over into the delivery measure nor the acid to be sucked back into the flask. The distillate is cooled and an aliquot portion titrated with one-tenth normal alkali, using methyl orange. The number of cc. of alkali required for the whole 20 cc. of acid deducted from 20 gives the number of cc. of acid neutralized by the ammonia. Each cc. of this neutralized acid corresponds to .00139 gm. of nitrogen, and the figure thus obtained multiplied by 556 and divided by the weight of paper taken gives at once the percentage of "bone-dry" gelatin present. In the case of casein the factor is 490.

A blank experiment using a paper free from gelatin should in all cases be done side by side with the above for the purpose of testing the reagents, etc. (even the air of the laboratory may invalidate the results by the presence of ammonia). Any neutralization of acid obtained in the "blank" must be deducted from the figure obtained in the main experiment.

The difficulties in carrying out an accurate determination of rosin in paper are great. Many methods have been proposed, but most of them are more or less unreliable. The simplest is perhaps that based on the turbidity produced on diluting an alcoholic solution of rosin with a considerable bulk of water. The paper under examination is extracted with alcohol and the extract poured into water in a tall glass cylinder. An opalescent turbidity is produced, due to the precipitation of free rosin, which turbidity is compared with that produced by an alcoholic solution containing a known weight of rosin. The results obtained by this method are very variable, since other bodies liable to be present are precipitated at the same time—notably, fatty acids from the soap often used in manufacture. The presence of more than 6 parts of rosin in 100,000 is further said to interfere with the delicacy of the reaction.

In Schumann's method the rosin is extracted by digesting with dilute alkali, precipitated with dilute sulphuric acid, filtered off, washed, dried, and weighed. Owing to the difficulty in completely removing the alkaline resinate formed the method is unsatisfactory, giving low results. The alkali, like alcohol, also extracts other bodies besides rosin.

The following method has been recently proposed by C. F. Sammet of the Bureau of Chemistry, Washington, who claims the results to be within the experimental error of .2 per cent. Five grammes of paper are cut into strips, folded, and extracted in a Soxhlet

with acidified alcohol (100 cc. of 95 per cent alcohol with 15 cc. of a 5 per cent solution of acetic acid). The solvent is allowed to siphon over from six to twelve times, after which the alcoholic extract is washed into a beaker, evaporated to small bulk, taken up with 25 cc. of ether, and transferred to a separating funnel containing 150 cc. of distilled water and a little salt to prevent emulsification. The contents of the funnel are well shaken, the water drawn off, and the process repeated. The combined ether extracts are then washed with distilled water to remove water-soluble salts, and the washed extract transferred to a platinum dish, the ether evaporated, and the residue dried in the water oven at 98° to 100° C. for one hour exactly, after which it is cooled and weighed. Fatty and waxy matters removed in the process are in too small proportions to affect the accuracy of the result.

Wurster's method for the determination of starch consists in first extracting rosin by treatment of the paper with absolute alcohol, acidulated with hydrochloric acid, and then drying and weighing the paper. The latter is now boiled with a solution consisting of equal parts of alcohol and water, also acidulated with hydrochloric acid, dried, and again weighed. The difference in the weighings represents the starch present. The method is open to objection for the following reasons, viz.: Firstly, the alcohol extracts matter in excess of the rosin, and, secondly, the starch is probably never completely removed by any process of simple solution.

The most satisfactory plan yet devised consists in converting the starch into soluble sugars and then determining these. Two methods are available. In the first, the conversion is effected by means of malt extract or diastase, a weighed quantity of paper being first extracted with alcohol to remove rosin, dried, weighed, and then treated with malt extract at a temperature of about 60° C. for half an hour to an hour. The glucose and maltose formed may be estimated directly in the manner hereinafter described, or the paper may be carefully washed, dried, and again weighed, and the difference in the two weighings taken as starch.

The second method depends upon the power of dilute acids to convert starch into glucose. Five grammes of paper are boiled with 500 cc. of distilled water for thirty minutes, and then thoroughly pulped. Sulphuric acid is now added to the liquid in the proportion of 2 per cent of its weight, and the whole is heated on the water bath under a reflux condenser for three hours, or until the liquid gives no further blue color with dilute iodine solution. At the end of this time the liquid is filtered, a slight excess of caustic soda added, the filtrate made up to a liter, and 200 cc. taken for the direct estimation of sugar which may be performed either (1) gravimetrically or (2) volumetrically. Each process is on occasion useful and both will therefore be described. In each case the re-

agent used is Fehling's solution, which is prepared by dissolving 34.64 gm. of pure crystallized copper sulphate in distilled water and diluting to 500 cc., while 70 gm. of caustic soda and 180 gm. of recrystallized potassium sodium tartrate (Rochelle salt) are dissolved in about 100 cc. distilled water and the solution also diluted to 500 cc. The two solutions are mixed in equal proportions just before use. From this mixture the reducing sugars possess the power of precipitating red cuprous oxide in proportion to the amount of sugar present.

For the gravimetric estimation, to 20 cc. of Fehling's solution at the boil is added the 200 cc. of filtrate from the acid treatment of the paper, and the whole boiled for a further ten minutes. The red precipitate formed is filtered through a Gooch crucible, washed, ignited, and rapidly weighed as cupric oxide. The weight multiplied by .4535 gives the weight of glucose in the 200 cc. of filtrate. The amount of glucose in the whole liter of filtrate multiplied by .9 gives the weight of starch present in the 5 gm. of paper.

For the volumetric estimation, 10 cc. of Fehling's solution diluted with water are boiled in a beaker and while boiling, the sugar solution, of the same strength as in the gravimetric process, is run in from a burette until the blue color of the Fehling's solution is completely discharged. In practice it is not easy to determine the end point of the reaction, and it is therefore better to employ an indicator. For this purpose a drop of a solution of potassium ferrocyanide acidulated with acetic acid is placed on a white tile or spotted on a filter paper, followed by a drop of the liquid from the beaker. While any un-reduced copper remains in the latter, a brown precipitate, or stain, will be produced. The number of cc. of sugar solution used is then read off and will correspond to .05 gm. of glucose since this amount is the weight of glucose capable of completely reducing 10 cc. of Fehling's solution. The amount of starch present in the 5 gm. of paper is calculated as follows:

$$.05 \times 1,000 \times .9$$

No. of cc. of sugar sol. used.

COLORING MATTERS.

Smalts, existing as it does in high-class papers, usually without admixture with loading materials, can be estimated with sufficient accuracy by incinerating the paper, weighing the ash, and making a correction for the small proportion of the latter due to the fiber, etc. This proportion does not usually exceed 2 per cent.

The *ultramarines* are of variable and even doubtful composition, and are therefore best estimated by comparing the depth of color of the ash with that of standard mixtures of the pigment with known proportions of china clay.

Chrome yellow, *orange*, etc., also of variable composition, may be determined, if necessary, by estima-

ting the lead and chromium separately, and calculating the results to the nearest indicated composition. It is scarcely necessary here to describe the full gravimetric process as it is likely to be but rarely required. It will be sufficient to say that the lead is precipitated and estimated as the sulphate, and the chromium as chromic oxide.

Prussian blue may be determined approximately by estimating the iron by igniting the paper, fusing the ash with sodium carbonate, treating the fused product with hot water, filtering, and boiling the residue with dilute hydrochloric acid and a drop or two of nitric acid. The solution is then again filtered, and the iron and alumina precipitated with ammonia in the presence of a little ammonium chloride. The precipitate of iron and aluminum hydrates is washed, filtered off, and digested with excess of caustic soda, then filtered again and carefully washed. The residue, which consists entirely of iron, is washed, dried, ignited, and weighed as the oxide. This process also serves for the estimation of all other iron pigments except the natural colors, ochres, etc.

Oils and fats can be estimated by extracting with ether, evaporating the solvent, and weighing the residue.

Paraffin-wax—similarly to the above, using benzin or petroleum spirit.

Salicylic Acid—This substance is used as a preservative in papers required for wrapping foodstuffs. It is extractable with petroleum ether, and may be estimated in the solution by diluting the latter with an equal volume of 95 per cent alcohol and titrating with one-tenth normal alkali, using phenolphthalein as indicator. Each cc. of one-tenth normal caustic soda is equivalent to .0138 gm. of salicylic acid.

Carbolic Acid—The estimation of carbolic acid in carbolized wrapping paper is frequently required. Commercial carbolic acid consists chiefly of cresylic acid with higher phenols, but little real phenol being usually present. Since, however, cresol is probably as efficient an antiseptic and insecticide for ordinary purposes as phenol, the absence of the latter body is of little importance. Carbolic acid may contain tar oils, which are, however, quite inert. Naphthalene is also liable to be present.

For the estimation of commercial carbolic acid the bromine absorption method in use for the determination of phenol is valueless. The writer has found the following method, which is based on a process originally described by Muter, quite satisfactory:

From 10 to 20 gm. of paper (according to the probable proportion of acid present) are cut into pieces and extracted with a sufficient quantity of alcohol (95 per cent) in a Soxhlet. The extract is transferred to a basin, mixed with about half its volume of a 10 per cent solution of caustic soda, and the mixed liquids evaporated in the water bath to small bulk. Tar oils and naphthalene, if present, here separate out and may

be removed by filtration. The liquid is now transferred to a separating funnel and hydrochloric acid added cautiously and with gentle shaking until the liquid shows an acid reaction. Means should be taken to prevent the mixture becoming too hot during the process. A little brine is now added. The liberated tar acids rise to the surface of the liquid which also becomes milky from the precipitation of rosin. The whole is now set on one side for a short time to complete the separation of the layer of tar acids, after which the resinous liquid is drawn off as completely as possible. The residue of oil is shaken up with ether or petroleum spirit, transferred to a weighed flask, the solvent evaporated off, and the residue weighed.

Bleach Residues—Excessive quantities of chlorides are the chief indications of faulty treatment of bleach residues and of insufficient washing. For the estimation of soluble chlorides the paper is extracted with hot distilled water and the solution evaporated to small bulk. To the resulting liquid is added, while stirring, silver nitrate solution till no further precipitate occurs, followed by a little nitric acid. The precipitate is allowed to settle, and the clear liquid is decanted through a filter. The bulk of the residue is now carefully washed several times with boiling distilled water to free it from acid, and is finally collected on the filter, and the whole dried in the water oven. The chloride is scraped from the filter, transferred to a weighed crucible, and heated at a low temperature until it commences to fuse. The filter is ashed separately on the crucible lid, and the ash treated with a drop of *aqua regia*, the resulting chloride being dried and added to the residue in the crucible. The weight of chloride multiplied by .248 gives the total chlorine.

Alum—For the estimation of alum the paper is extracted with hot water, rendered slightly acid with a drop or two of sulphuric acid. The alumina is then precipitated with ammonia and estimated as described under "Loadings."

Acidity—The total acidity of a paper is estimated by titrating a distilled water extract with one-tenth normal alkali, using litmus as indicator.

Soluble Sulphur Compounds are determined by extraction with distilled water and titration with one-tenth normal iodine solution.

Arsenic—An estimation of this substance is occasionally required, as where it forms the base of a coloring matter, or as in flypapers, etc. Where a relatively large quantity is available and is present as arsenous acid (as it frequently is) it may be estimated by extracting with a boiling solution of sodium bicarbonate and titrating the extract with one-tenth normal iodine and starch. Each cc. of one-tenth normal iodine corresponds to .0049 gm. of arsenous acid. Where minute quantities of arsenic only are present (or available) the following process is necessary:

The paper is first heated for some time with a mix-

ture of sulphuric and nitric acids in the proportion of 30 parts to 1. The carbonized residue is boiled with distilled water and filtered. An apparatus is prepared consisting of a flask provided with a stoppered funnel and having an outlet connected to a drying tube containing calcium chloride, and leading to a hard-glass tube having a piece of wire gauze wrapped round it near the middle, and heated by a Bunsen under the gauze. The arsenic extract is introduced into the flask via the stoppered funnel after 2 to 3 gm. of arsenic, free zinc, and some *pure* hydrochloric acid have been placed in the flask. A mixture of arsenuretted hydrogen and hydrogen is evolved which is split up on reaching the heated portion of the tube and deposits a mirror of metallic arsenic in the cooler portion of the tube. This mirror is compared with those produced by solutions containing known amounts of arsenic. A "blank" experiment must always be performed in order to test the purity of the reagents.

POSITION OF INDIAN JUTE INDUSTRY.*

In view of rumors prevailing in the country districts regarding the effect of the European war on the Indian jute industry, the Bengal Government prepared a statement regarding the present position of jute, and has given it wide circulation.

The notice states that of the 1912-13 exports of raw jute from India the British Empire took some 341,000 bales and foreign countries 535,000 bales; of the gunny bags shipped in that year the British Empire purchased 107,600,000 and foreign countries 205,000,000; of the gunny cloth exported, 118,000,000 yards went to the British Empire and 904,000,000 yards to foreign countries; and in addition the British Empire absorbed \$18,079,048 worth of India's jute manufactures and foreign countries took \$56,120,478 worth.

The distribution of these exports among the chief countries is shown in Table I:

The chief points of interest brought out by these figures are that Germany and Austria take more than one-fourth of India's exports of raw jute, but as a customer for gunnies they, and indeed the continent of Europe as a whole, are comparatively insignificant; and that India's best customers are the United Kingdom, the United States, Argentina, Chile, and Australia, which take more than half the raw jute exports and four-fifths of the gunnies. The war should not interfere materially with the trade in gunnies; it will, however, stop the export of 230,000 tons of raw jute to Germany and Austria.

A firm of brokers issued a statement of the position of jute as of July 31, 1914, in which the arrivals at

Calcutta from July 1 to 31 were estimated at 186,000 bales of 400 pounds net, this amount including 50,000 bales brought forward from the season ended June 30, 1914. Exports for the month from Calcutta and Chittagong were placed at 80,000 bales, the purchases of Calcutta mills at 56,000, and the estimated stocks on hand in the bazaars, press houses, etc., as of July 31 at 50,000 bales.

TABLE I.

Countries.	Raw jute. Tons.	Gunny bags. Number.	Gunny cloth. Yards.	Manufac- tures.
United Kingdom	340,000	27,000,000	41,000,000	\$ 4,832,435
Straits Settle- ments		9,000,000	215,000	1,060,897
South Africa....		51,000,000	1,500,000	1,946,600
Canada		2,420,000	50,000,000	2,433,250
Australia and New Zealand.		47,000,000	23,000,000	6,813,100
Austria-Hungary	52,000	970,000	95,000	97,330
Belgium		4,000,000	66,000	394,186
France	86,000	935,000		30,440
Germany	180,000	6,000,000	3,000,000	705,643
Turkey		3,500,000	2,000,000	535,315
Other Europe ..	76,000	5,000,000	700,000	535,315
United States ..	124,000	43,000,000	663,000,000	29,199,000
Argentina and Chile		600,000	217,000,000	12,652,900
China		19,000,000	3,000,000	2,433,250
Egypt		14,000,000	1,000,000	1,824,938

Regarding the position of the Calcutta mills the firm referred to estimated the stocks on hand June 30 at 1,400,000 bales and the purchases during July, as stated, at 56,000. The Indian Jute Mills Association estimates the consumption of the Calcutta mills during the current (1914-15) year at 4,743,000 bales (against an actual total consumption of 4,444,000 bales in 1913-14), on the basis of short time to September 30 and full working time from that date until the end of the jute year.

According to a local publication, the crop is being allowed to deteriorate through becoming overripe. Reports have been circulated among the farmers that there was no demand for their crops, with the result that harvesting is practically at a standstill. The Government is being urged to come to the assistance of the industry by disseminating the information in every village in southern Bengal where jute is grown that there is a sale for the fiber and by advocating the immediate harvest of the crop. The main hope for the jute crop lies in the possibility of the mills purchasing, which at the present time depends to a great extent on their getting sufficient tonnage to ship their stock of gunnies and cloth, which has mostly all been sold, and their daily production, which has been sold for some months forward. But in any case they should be able to purchase this year's excess, the major portion of which they may not be able to consume until 1916. They will only do so at their own price, in setting which they will, of course, have to take into account the fact that jute will deteriorate in quality the longer it is stored.

*From Daily Consular and Trade Reports.

METALLURGY.

MICROSCOPIC STRUCTURE OF HIGH SPEED STEELS.

By H. B. PULSIFER.

(Continued from November issue.)

After heating the specimens to 920° C. in the furnace the temperature was held at that point for ten minutes and one piece of each variety, A, B, C, D, E and F, was withdrawn and quenched in the strong air

blast. Steel A, quenched from 980° C. (Fig. 1) shows less carbide while the pearlite and crinkly spots are more sharply defined. This specimen shows that the crinkly field is the typical structure of the quenched steel while the pearlite fills in the spaces about the less differentiated areas. Shall we call the harder spots troostite or martensite? In the literature we find pearlite, sorbite, troostite, martensite and austenite applied to the structures of this class of steels. Because of its dis-

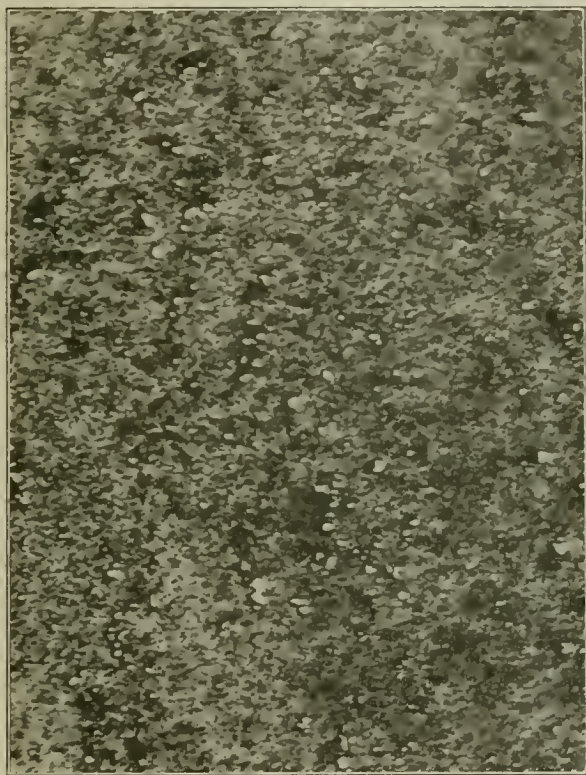


Fig. 1.

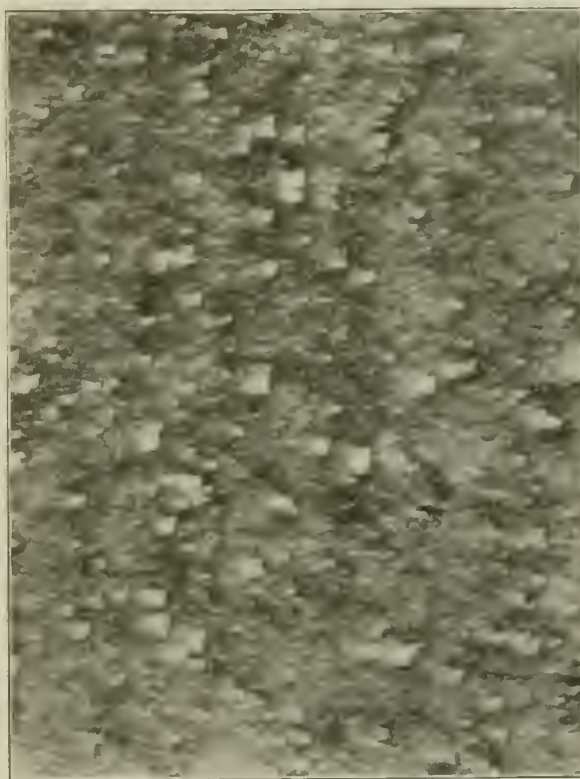


Fig. 2.

blast. The same was repeated by raising the temperature to 980° C. and withdrawing still another series. Illustrations of the structures found are reproduced in the seven cuts accompanying.

Steel A, quenched from 920° , is heavily attacked by picric and nitric acids, as well as sulphurous acid; the structure of the annealed condition is found as well as one characteristic of quenched high speed steels. The droplets of carbide persist, quite as in softened steels; the pearlite is also conspicuous but now, instead of constituting the whole ground, lies only between fine crinkly-lined tracts. In spots the pearlite is quite as granular as in the annealed specimens; the new areas resemble pearlite but are not as well defined and corrode less, as if the white component of pearlite predominates. The structure is very fine.

tinctly granular texture, although often so fine as to resolve with difficulty, and because of similarity in etching and play of colors we have elected to call the structure of the annealed specimens "pearlitic." "Sorbitic" is a term used for structures of about this degree of heterogeneity from solid solutions or progress toward the easily corroded and sizable granularity of typical pearlite. "Troostite" appears likewise best relegated from use in this connection because of inability to distinguish it from its earlier (martensitic) or later (sorbite) transition products. We therefore call the hard, crinkly areas "martensite."

Steel B, quenched from both 920° and 980° shows plenty of the carbide droplets and general martensitic groundmass. Picric and nitric, as well as sulphurous acid, attacks without difficulty; the field appears gran-

ular after etching but gentle repolish restores a rather bright, crinkly surface much different from pearlite. Fig. 2 is of the one quenched at 980° ; both steels are hard, spots on the 980° specimen attaining 86 on the sclerscope scale.

Steel C, as quenched from both temperatures, has quite similar appearance. In the annealed condition

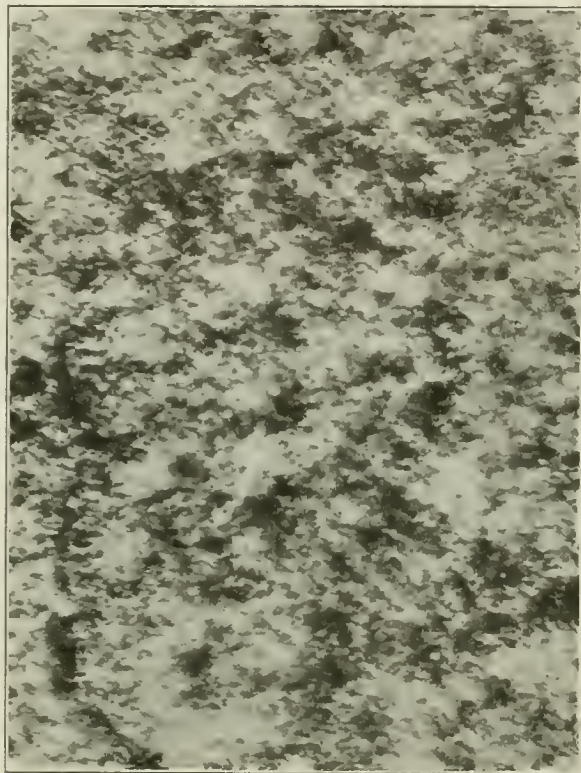


Fig. 3.

this steel has less carbide than any of the others; all the quenched specimens show uniformly slight amounts of carbide, scarcely a single dot of carbide is seen in either specimen. Both are almost identical and Fig. 3 is of the one hardened from 920° . These two specimens are somewhat softer than steel B yet etch with more difficulty. It is true that the carbon is least in this steel but only slightly less than the others; the higher chromium might be expected to bring out carbide even with less total carbon, but such is not the fact. Leon Guillet, who has investigated high-speed steels with more success than most men, says that maximum hardness is associated with total disappearance of the carbide*; there is certainly no exceptional hardness in these two specimens which are exceptionally free from that constituent.

Steel D, quenched at 920° and 980° (Fig. 4) gives rather dissimilar results for the two temperatures. The first appears like a pearlitic steel, the second martensitic and like most of the quenched samples. The first has numerous carbide globules, the second practically none. The first etches like pearlitic structure,

the second like martensite. With the sclerscope the second is slightly harder than the first but the first is far harder than any of the annealed specimens. It is admitted that the control in the heat treatment of the specimens was not as rigorously carried out as should have been the case; with that granted, it is difficult to correlate the facts of structure, etching and hardness. The hardness is similar but the structures quite different; further repolish might brighten up the structure of the 920° specimen but it could not eradicate the abundant globules of carbide. It is noticeable that the martensitic structures may tarnish dark but brighten with repolish while the pearlitic structures corrode more easily and are brought to a smooth surface again only with much effort.

Steel E. If the appearance of the two previous specimens is difficult to explain that of steel E quenched at 920° is impossible. The section exposed by grinding one side of the specimen shows a core of martensite surrounded by a pearlitic zone, outside of which

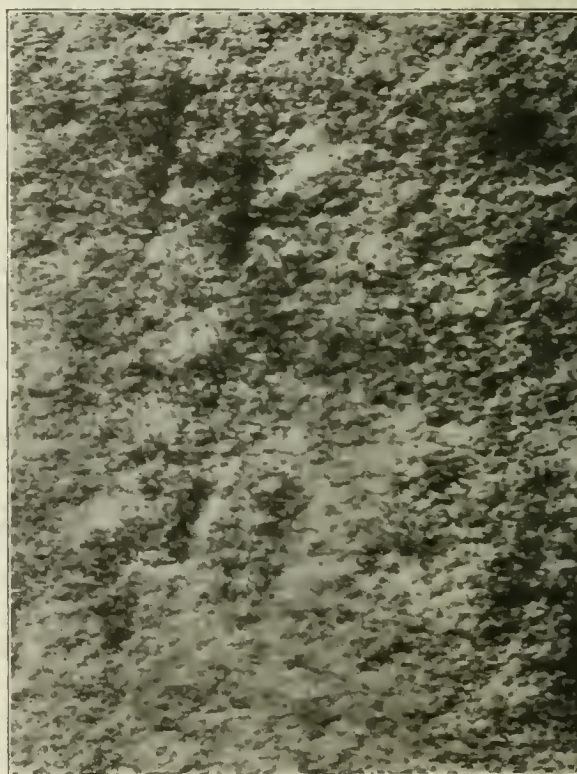


Fig. 4.

is an exterior shell of cellular austenite. Fig. 5 shows a bit of the field where the cellular structure is of medium grain. Many of the specimens heated to the higher temperatures developed this cellular structure; none, however, this structure at so low a temperature as this one. The cellular nature is well known and commonly spoken of as "austinitic"; in its resistance to etching, striated surface and softness it is closely related to the austenite of the carbon steels. Where the core of this specimen is of the martensitic appearance it has hardness from 65 to 76 and no cellular

*Journal Iron & Steel Institute; LXX; 1906, II; p. 127.

lines apparent. Fig. 5 is of the finer and inner layer of the austenite, the coarse, huge grains of the more exterior portions will be shown in a later figure.

Steel E, quenched at 980°, has what might be expected for normal structure as heated to and quickly cooled from this temperature. It contains carbide



Fig. 5.

droplets, pearlitic patches and a general field of martensite; it does not appear different from steel B quenched at the same temperature (Fig. 2.). As will be seen later steel E develops this cellular structure more easily than any of the others; in fact, five of the seven hardened specimens display this nature; we may, for this reason, be excused from attempting to account for the anomaly.

Steel F, samples of which were hardened from 920° and 980°, shows peculiar results. Fig. 6 is a good illustration of the appearance shown from the lower quenching; the specimen etches easily and is conspicuously like annealed material; that is, uniformly pearlitic with droplets of carbide. The surface of this specimen is entirely uniform and the scleroscope indicates hardness from 44 to 47, distinctly higher than in any of the annealed specimens and over twice the hardness of its own annealed sample. Fig. 7 is of the specimen quenched at 980°; this specimen etched slowly with both agents, the surface appears less differentiated than the one from 920° but its hardness is distinctly less, from 27 to 37 with most readings around 30. Here we have the appearance and etching of a hardened steel without its proper hardness.

Quenched from 920° in Air Blast.

Hardness,
Scleroscope, 9 tests.

Etching Test.

Etching Test.			Low.	Mean.	High.
Steel.	Picric+Nitric.	SO ₂ .			
A	Strong Attack	Strong Attack	41	45	47
B	Strong Attack	Strong Attack	55	74	82
C	Easily Etched	Easily Etched	57	64	68
D	Easily Etched	Easily Etched	42	55	64
E	Core-Slight Attack	Light Attack	65	70	76
F	Easily Etched	Easily Etched	44	45	47
Quenched from 980° in Air Blast.					
A	Strong Attack	Strong Attack	48	56	62
B	Easily Etched	Easily Etched	74	77	86
C	Slight Effect	Easily Etched	58	72	78
D	Easily Etched	Easily Etched	51	60	68
E	Easily Etched	Easily Etched	44	52	60
F	Slow Attack	Slow Attack	27	30	37

The specimens quenched at 920° and 980° show plainly the three most distinct types of structure—pearlitic, martensitic and austenitic. The samples displayed indicate the mixed pearlitic and martensitic types, with and without globules of carbide. The sample with cellular grain, which we call austenitic mainly because of this grain, has abundant striations within each cell boundary; this latter, together with the great hardness might indicate that the structure is really martensitic instead of austenitic. As a matter of fact,



Fig. 6.

Leon Guillet, in the paper already cited, speaks of similar polyhedra filled with extremely fine martensite. The heavy pitting so noticeable in our Fig. 5 has been brought to attention by H. C. H. Carpenter in particular, explanation of which may better be deferred until later, when more exaggerated examples will be shown.

Some of these quenched specimens have a remarkable tendency to tarnish on drying after the etching and repolish. If such coloring is allowed to take place all sorts of banded, striated and spotted appearances may develop. Our drying is done with alcohol and absorbent cotton, after which the specimen is put in a dessicator and kept from the air as much as possible. Our Fig. 4 is somewhat defective this way but we be-

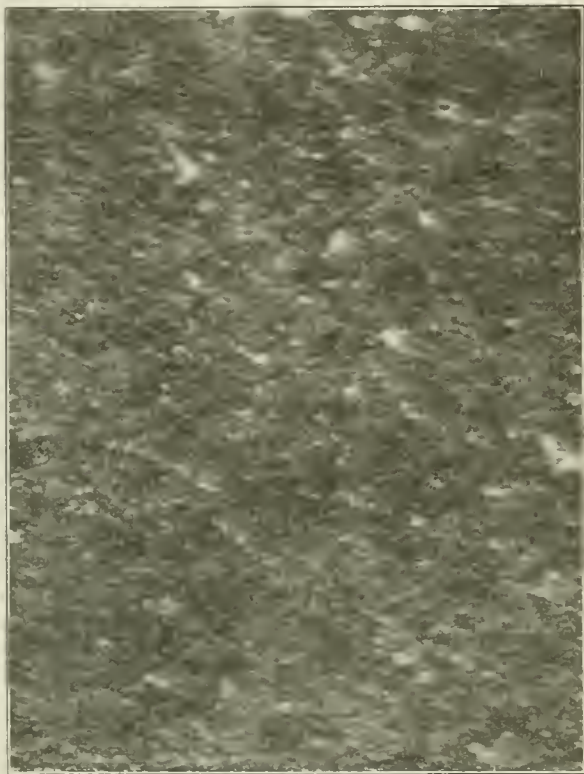


Fig. 7.

lieve that in the main the prints are free from such error.

In recognizing the three main structures with their mixtures and accompanying constituents we are apparently at the limit of the method employed. Further differentiation is patently desirable from the great inability of such structures to account for the properties otherwise possessed.

The chemical industry has created a big market for Norwegian pyrite, which, owing to its small arsenic content, commands a higher price than the Spanish. The market for this product is generally England, Germany, France, Sweden, and other European countries. The Lokken mines, at Meldalen, the largest sulphur pyrite mines in Norway, operated by a company composed of Norwegian, Swedish, German and English stockholders, showed excellent results from the 1913 operation. This mine was started with a capital of \$536,000, which was gradually augmented to \$1,876,000, and in December, 1913, the capital was increased to \$3,752,000. A net profit of \$402,000 was shown from the year's operations, and a dividend of 5 per cent was declared.

AGRICULTURAL USE OF LIME.

The use of lime as a fertilizer dates from the inception of modern scientific farming. Agricultural chemists have shown that there are five or six different functions which lime may perform to benefit a soil, which may be summarized briefly as follows:

1. It is an essential element of plant food.
2. It aids in the conversion of decaying organic matter into humus.
3. It forms compounds with the humic acids which tend to prevent their being leached out of the soil and lost.
4. By producing proper sanitary conditions the growth of injurious bacteria is largely prevented, while the growth of nitrifying bacteria is encouraged. These nitrifying bacteria convert the nitrogen of the humus into such a form that it is available as a plant food.
5. Lime aids in the liberation of potash and phosphorus from inert compounds.
6. It tends to flocculate clay soils, rendering them granular and more porous.

Obviously, permanent results cannot be expected unless care is taken to insure the presence of some organic fertilizer at all times. Lime used alone may be temporarily beneficial but will eventually be harmful; when used with cowpea vines it becomes more efficient for general purposes than almost any other fertilizer. Of course, lime is not beneficial to all crops to the same extent, and not all soils need lime. Thus, some of the common plants which are stated by the Department of Agriculture to be benefited by lime, are spinach, lettuce, beet, celery, onion, cucumber, cantaloupe, asparagus, cabbage, peanut, rhubarb, pea, pumpkin, bean, tobacco, alfalfa, clover, barley, wheat, oats, timothy, gooseberry, currant, orange, quince, and cherry. Indian corn is only slightly benefited.

Plants which are said to be slightly injured by lime are cotton, tomato, cowpea, concord grape, peach, apple, and pear, and those really injured are radish, flax, blackberry, black raspberry, and cranberry.

Whether a soil will respond to liming or not depends on the amount of available calcium oxide which it already contains. Probably the best indication of the need of lime is the failure to obtain a good crop of clover.

The question whether lime should be applied to the soil as quicklime, hydrated lime, air-slaked lime, or ground limestone is still the subject of a great deal of controversy. The advocates of ground limestone claim that the caustic properties of quick or hydrated lime will burn up and destroy the organic matter in the soil, whereas limestone can be applied in large quantities at long intervals and will therefore produce a more or less permanent fertility. The advocates of lime claim that one of the main functions which lime has to perform is the destruction of the organic matter and the liberation of the nitrogen in such a form that the plant can use it.

The CHEMICAL ENGINEER

HARRY McCORMACK, Editor.

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NOTES AND COMMENT.

Analyses of Coal.

The United States Bureau of Mines has just issued a small edition of Bulletin 85, "Analyses of Mine and Car Samples of Coal Collected in the Fiscal Years 1911 to 1913," by Arno C. Fieldner, Howard I. Smith, Albert H. Fay and Samuel Sanford. The present bulletin presents analyses and descriptions of samples of coal collected from many mines throughout the entire country. In order that the material in this bulletin may be made to supplement that presented in Bulletin 22, "Analyses of Coals in the United States," the same plan of geographical classification has been followed, the analyses and descriptions of the samples being grouped in alphabetical order according to the state, county, and town near which the mines or prospects sampled are situated. Bulletin 22 was said to be the most comprehensive publication ever issued on the coals of the United States and the new bulletin is an extension of that work. So great was the demand for Bulletin 22, the free edition was exhausted a few weeks after its issuance. At the present time the only way to obtain a copy of Bulletin 22 is through the Superintendent of Documents, Government Printing Office, Washington, D. C., who sells the publication at eighty-five cents. In Bulletin 85 are chapters on the collection of samples, the method of mine sampling fol-

lowed by the Bureau of Mines, the relation of mine samples to commercial shipments, methods for the determination of moisture, ash, volatile matter, fixed carbon, and sulphur.

U. S. Geological Survey as Clearing House.

The war in Europe has developed at least one new line of governmental activity wherein the United States Geological Survey is now acting as a bureau of information and clearing house for over 90,000 American mineral producers and manufacturers. The interference with shipping on the beginning of hostilities called sharp attention to the fact that the United States had been importing many minerals and mineral products the raw materials of which exist in large and workable deposits in the United States. It had been, however, a little easier, or possibly a little cheaper, to import such ores than to develop them at home. The shutting off of the imports immediately raised such questions as "Have we magnesite?" or "Have we ferromanganese?" or "What clays have we in the United States?" and the public statements at once given out by Secretary of the Interior Lane and by the Geological Survey regarding our American mineral reserves naturally resulted in inquiries from thousands of American firms. A heavy correspondence has grown out of this condition, and often a single mail brings requests from certain manufacturers to be placed in touch with producers of raw material, and also statements from the producers themselves that they are ready to supply the demand for raw material. Like many business offices, the Geological Survey places a file number on each letter as it is received, and it is an interesting coincidence that the other day a letter which was stamped No. 371353 was from a firm of wholesale druggists asking for the names of manufacturers who are taking up the subject of making from American petroleum the medicinal oils formerly imported from Russia, while the very next letter, No. 371354, was from an oil-refining company stating that while this company had been the largest importer of oils of this character immediately after the war it equipped its plant and is now producing oil equal to the product formerly imported, a sample of the American product being forwarded for inspection. It is now a daily occurrence for the Geological Survey to answer scores of letters from consumers inquiring for the names of the producers of particular articles. The names furnished in reply to an inquiry of this sort may be only one or two or may comprise as many as 200 or 250.

Inspecting Fire Hazards.

The Committee on Field Practice of the National Fire Protection Association has completed its two years' work in the compilation of an inspection manual. This publication is called Field Practice to distinguish it from an ordinary fire protection hand book, from

which it differs radically in function. It is not a mere compilation of fire protection standards, but a handbook designed to educate and serve the man who is undertaking inspection work, and who, possibly, has had very little previous experience. The increasing inspection of premises by uniformed members of the fire departments and by newly constituted municipal inspection bureaus has made such a handbook imperative, covering not only standard equipments, but covering what may be called points of relaxation from the standard which the inexperienced inspector does not know how to look for. This book is designed to point out the common faults in equipments and those points of deterioration difficult for inexperienced persons to discover, with methods and suggestions for their remedy. It is, in its potential usefulness, the most important publication which the National Fire Protection Association has ever compiled.

RECENT PATENTS.

The following patents relating to industrial and engineering chemistry are reported by C. L. Parker, solicitor of chemical patents, McGill Building, Washington, D. C.

1,112,547. Composition of Matter to Be Used as an Oxygenizer in Connection with Combustibles. Adolphe Morin and Ernest Hess, Montreal, Quebec, Canada. Patented Oct. 6, 1914.

1,112,602. Process of Treating Mineral Oils. Julius Dehnst, Halensee, near Berlin, Germany. Patented Oct. 6, 1914.

1,112,650. Process of Treating Fullers Earth. Charles L. Parsons, Durham, N. H. Patented Oct. 6, 1914.

1,112,853. Manufacture of Zinc Oxid. James Arthur Singmaster, Palmerton, Penn. Patented Oct. 6, 1914.

1,112,887. Process for the Recovery of Pulp from Waste Papers. John M. Durby, Astoria, New York. Patented Oct. 6, 1914.

1,112,893. Making of Alkali Cyanogen Compounds. John Collins Clancy, Colorado Springs, Colo. Patented Oct. 6, 1914.

1,112,909. Process of Converting Castiron into Steel or Malleable Iron. John Alexander Hunter, Philadelphia, Pa. Patented Oct. 6, 1914.

1,112,938. Process for the Improvement of Inferior Grade Rubbers. David Spence and William F. Russell, Akron, Ohio. Patented Oct. 6, 1914.

1,113,096. Process of Producing Hydrogen. Carl Bosch and Wilhelm Wild, Ludwigshafen-on-the-Rhine, Germany. Patented Oct. 6, 1914.

1,113,112. Process of Hardening Concrete Structure. Sylvester W. Flesheim, Cleveland, O. Patented Oct. 6, 1914.

1,113,123. Apparatus for Producing Lead Oxid, William Innes, Liverpool, England. Patented Oct. 6, 1914.

1,113,151. Apparatus for Making Lard Substitute. Jesse C. Chisholm, Dallas, Texas. Patented Oct. 6, 1914.

1,113,178. Process of Producing Barium and Strontium Oxids. Harry G. Akers, Toronto, Ontario, Canada. Patented Oct. 13, 1914.

1,113,275. Process of Varying the Velocity of Detonation of Explosives. Clifford A. Woodbury, Chester, Pa. Patented Oct. 13, 1914.

1,113,323. Treatment of Refractory Ores. John Foye, Henry Egbert Moore and Robert Boyle, Johannesburg, Transvaal, South Africa. Patented Oct. 13, 1914.

1,113,491. Process of Detinning, Wallace Savage, Piedmont, Ala. Patented Oct. 13, 1914.

1,113,539. Manufacture of Manganese Steel. William Campbell, New York, N. Y.; John H. Hall, High Bridge, N. J., and Henry H. Howe, Bedford Station, N. Y. Patented Oct. 13, 1914.

1,113,546. Electrolyte for Use in Electro-Metallurgy. Nicholas Henri Marie Dekker, Paris, France. Patented Oct. 13, 1914.

1,113,598. Method of Fixing Nitrogen. John E. Bucher, Coventry, R. I. Patented Oct. 13, 1914.

1,113,630. Process for the Production of Caoutchouc Substances. Fritz Hoffmann and Carl Coutelle, Elberfeld, Germany. Patented Oct. 13, 1914.

1,113,759. Colored Caoutchouc Substances and Process of Making Same. Rudolf Ditmar, Gratz, Austria-Hungary. Patented Oct. 13, 1914.

1,113,782. Fireproof and Wood Preserving Paint. James W. Grimes, Springfield, Ohio. Patented Oct. 13, 1914.

1,113,927. Process of Manufacturing Acetic Anhydrid. Wallace A. Beatty, New York, N. Y. Patented Oct. 13, 1914.

1,114,017. Process of Manufacturing Alcohol from Garbage. James J. Morgan, Chicago, Ill. Patented Oct. 20, 1914.

1,114,067. Treatment of Oils, Fats and the Like. Nils Testrup, London, England. Patented Oct. 20, 1914.

1,114,119. Finishing Composition and Method of Preparing Same. Michael F. Coughlin, Stoughton, Mass. Patented Oct. 20, 1914.

1,114,278. Treating Rosin. Frank E. Mariner, Gull Point, Florida. Patented Oct. 20, 1914.

1,114,372. Process of Roasting Ores. Frederick Laist, Anaconda, Mont. Patented Oct. 20, 1914.

1,114,446. Refractory Material. James R. Campbell, Scottdale, Pa. Patented Oct. 20, 1914.

CHEMICAL ENGINEER

Diplom-Ingenieur desires work. Lately engaged with a Canadian gas company, but dismissed, being an Austro-Hungarian subject. Has best references, aged 29. Perfect and reliable analyst. Experienced in research work in the manufacture of charcoal, wood-distillation by-products, acetone, formaldehyde, heavy chemicals, alumina, sulphate of alumina, copper and zinc ore extraction and acid nitric from the air. (L. Zender's fuel process, now applied on practical scale for natural gas off Kissávmás in Austria-Hungary).—S. S., Care of THE CHEMICAL ENGINEER.

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